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POLYCYCLIC AROMATIC HYDROCARBONS IN THE AQUATIC ENVIRONMENT

FORMATION, SOURCES, FATE AND EFFECTS ON AQUATIC BIOTA

NRCC No. 18981

ASSOCIATE COMMITTEE ON SCIENTIFIC CRITERIA FOR ENVIRONMENTAL QUALITY

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LES HYDROCARBURES AROMATIQUES POLYCYCLIQUES DANS LE MILIEU AQUATIQUE: FORMATION, SOURCES, DEVENIR ET EFFETS SUR LE BIOTE AQUATIQUE

Les hydrocarbures aromatiques polycycliques (HAP) constituent un groupe important et diversifié de composés de masse moléculaire élevée possédant au moins deux noyaux aromatiques. On trouve ces hydrocarbures et des substances chimiques apparentées dans de nombreux milieux environnementaux. On attribue leur présence à des processus naturels ou anthropiques. En ce qui concerne l'écologie et la santé, on se préoccupe surtout des HAP qui, soupçonne-t-on, pourraient être cancérogènes ou mutagènes.

Le rapport résume les propriétés physiques et chimiques des HAP applicables à l'environnement. Il étudie leur source et leur dynamique environnementale et, dans certains cas, leur mode de pénétration et leur devenir dans les écosystèmes aquatiques. Il se termine par une étude critique des effets toxicologiques et environnementaux des HAP sur le biote aquatique.

Le groupe d'experts qui a préparé ce rapport signale des lacunes importantes dans les bases de données actuellement accessibles; il fait plusieurs recommandations sur la façon d'obtenir les connaissances scientifiques nécessaires pour combler ces lacunes. Le rapport comprend aussi un bref résumé et un index détaillé des sujets traités.

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ANNOUNCEMENT
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POLYCYCLIC AROMATIC HYDROCARBONS IN THE AQUATIC ENVIRONMENT: FORMATION, SOURCES, FATE AND EFFECTS ON AQUATIC BIOTA

Polycyclic aromatic hydrocarbons (PAHs) are a large and diverse group of high-molecular-weight compounds having two or more aromatic rings. These hydrocarbons and related chemicals have been identified in numerous environmental media, and their presence has been attributed to both natural and human activities. Of major concern from a health and ecological perspective are the PAHs that are suspected of being potentially carcinogenic or mutagenic.

This report summarizes those physical and chemical properties of PAHs that are of relevance to environmental situations. It examines the sources of these compounds as well as their environmental dynamics, and in particular their mode of entry and fate in aquatic ecosystems. The report concludes with a critical examination of the toxicological and environmental effects of PAHs on aquatic biota.

The expert panel of authors note important gaps in the scientific data base currently available, and they make several recommendations aimed at obtaining the scientific knowledge needed to fill those gaps. A concise summary and an extensive subject index are also contained in this report.

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POLYCYCLIC AROMATIC HYDROCARBONS IN THE AQUATIC ENVIRONMENT: FORMATION, SOURCES, FATE AND EFFECTS ON AQUATIC BIOTA

PANEL ON POLYCYCLIC AROMATIC HYDROCARBONS
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SUMMARY

1. NOMENCLATURE, STRUCTURE, AND PHYSICAL-CHEMICAL PROPERTIES (see Sections 2.1 to 2.3)

Polycyclic organic matter (POM) is a general designation for a large and diverse group of chemicals having two or more aromatic rings. Of major concern from a health and ecological perspective are the carcinogenic polycyclic (polynuclear) aromatic hydrocarbons (PAHs) and their nitrogen analogues (aza and imino arenes). For the purposes of this report, only compounds containing three or more fused aromatic rings are examined in detail. Information on smaller compounds (e.g. naphthalene and its derivatives) is included for comparative purposes. It is recognized that in recent years increasing attention has been focused on heterocyclic aromatic compounds (HACs) - compounds containing nitrogen, oxygen, sulfur - and in particular on those aromatic compounds containing nitrogen. As yet, the scientific data base is insufficient to assess the potential health and environmental effects of these particular compounds; however, the available information on heterocyclic aromatic compounds is included. When sufficient information has been generated, a separate and detailed examination of these compounds should be undertaken.

The PAHs discussed in this report have molecular weights ranging from 166 to greater than 328, melting points above 100°C and boiling points above 300°C. They usually have low vapor pressures (10^{-5} to 10^{-13} kPa at 25°C) and low water solubilities (< 1 $\mu g.L^{-1}$ to 1 $mg.L^{-1}$), are hydrophobic and have high affinities for particle surfaces. Compounds having fewer than three aromatic rings (i.e. PAHs of low molecular weight) are usually more volatile and more soluble in water than those with more than three aromatic rings (i.e. high molecular weight PAHs). However, such a division in physical properties is not distinct since these properties may be dramatically influenced by such factors as the geometric orientation of the aromatic ring and the degree of substitution.

In oxidizing environments, PAHs may react readily to form water-soluble compounds. Nitration and sulfuration of PAHs have also been demonstrated.

2. DETERMINATION OF PAHs IN ENVIRONMENTAL SAMPLES (see Section 2.4)

Numerous analytical techniques have been developed to analyze PAHs in various environmental matrices. These techniques range from relatively simple and rapid semi-quantitative methods to elaborate, expensive and time-consuming quantitative analyses. Because PAHs are usually found in low concentrations in environmental samples and are associated with similar and interfering chemicals, extensive and often inappropriate alterations of the samples very frequently occur prior to

the actual analysis. Serious reservations have been expressed regarding the adequacy of the data base with respect to environmental levels of PAHs, especially when factors such as sample contamination and artifact formation have not been thoroughly considered. As a result, a relatively small amount of information on the actual environmental levels of PAHs is contained in this report. A detailed assessment of the sampling and analysis methodologies for PAHs is beyond the scope of this report; a separate examination of this topic should be undertaken.

3. ENVIRONMENTAL DYNAMICS (see Chapter 3.0)

Polycyclic aromatic hydrocarbons enter the aquatic environment via 1) the deposition of material originally released to the atmosphere and subsequently deposited on surface waters or land, and 2) the direct and indirect release of material in surface and ground waters. These two general routes of entry are responsible for both the background levels of PAHs recorded at sites removed from identifiable sources, and the elevated levels associated with site-specific sources.

3.1 FORMATION (see Section 3.1)

Complex mixtures of PAHs are formed by the incomplete/inefficient combustion of organic materials, by diagenesis, or by biosynthesis. The relative rates and extent of formation depend upon the particular process. The feedstock and temperature of combustion play a significant role in determining the abundance and chemical complexity of the resulting PAH mixtures. Although limited information is available, the maximal yields of the individual PAHs are apparently produced at significantly different combustion temperatures.

Temperature also plays a role in the chemical complexity of the PAHs produced during combustion. At very high temperatures (2000°C) the PAH mixture contains predominantly unalkylated compounds and some compounds with a small degree of alkylation. At intermediate temperatures (400-800°C), substantial quantities of alkylated PAHs are formed. Recent field observations have led researchers to speculate that the presence of PAH-mixtures in recent marine and freshwater sediments is partially attributable to the combustion of organic materials at high and intermediate temperatures with subsequent atmospheric transport and deposition. The slow transformation at low temperatures (< 150°C) of PAH precursors (i.e. diagenesis) leads to extensive alkyl and cycloalkyl substitution and to low relative abundance of unalkylated PAHs; such extensive alkylation has been observed in ancient sediments and in crude and shale oils.

A large number of biosynthetically-produced PAH precursor compounds have been identified and it is postulated that some PAHs are produced by the transformation of such biogenic material in sediments.

The complete biosynthesis of PAHs has not been unequivocally demonstrated. Although certain microorganisms and plants appear capable of synthesizing some PAHs under laboratory conditions, the possibility of contamination in such studies has not been adequately investigated.

3.2 SOURCES (see Section 3.2)

Atmospheric

Considerable attention has focused on the release of PAHs to the atmosphere via combustion, pyrolysis, vaporization and/or aerosolization. Virtually any combustion process using organic fuel has the capacity to generate PAH compounds. Of particular importance are (1) industrial processes: coke production, catalytic cracking of crude oil, and aluminum smelting; (2) fuel combustion from such stationary sources as fossil-fueled power plants and residential and commercial space heating; (3) transportation sources such as gasoline- and diesel-powered motor vehicles; (4) solid waste incineration; and (5) non-industrial combustion such as forest fires and agricultural burning. The relative importance of such sources depends upon the fuel used, the operating and meteorological conditions, and the sensitivity of receptors.

There is currently no national inventory of PAH emissions for Canada, although some information is available for the Province of Ontario and for the United States. The Ontario Ministry of the Environment, using emission factors developed in the United States, identified forest fires and open burning as the most significant contributors to total atmospheric loading. Studies in the United States have indicated that residential space heating and open burning are the two largest contributors to total atmospheric loading, with transportation, coke production, and aluminum smelting also contributing significant amounts on a national scale.

Waterborne

Various amounts of PAHs enter the aquatic environment in municipal and industrial effluents, and surface runoff also probably contributes substantially to the PAH loading of effluents. The normal use of materials produced by pyrolysis (e.g. coal tar, creosote, anthracene oil, coal tar pitch, petroleum pitch, carbon black, crankcase oil, etc.) along with their intentional or accidental release, may result in elevated levels of PAHs in the aquatic environment.

3.3 ENTRY INTO THE AQUATIC ENVIRONMENT (see Section 3.3)

The identification of PAHs in marine and freshwater sediments and some aquatic biota has led many authors to speculate that

atmospheric deposition is a significant route of entry into the aquatic environment and is responsible for much of the background concentration of PAHs. Water- and land-based discharges contribute significant amounts of PAHs in specific locales and thus, may augment background concentrations.

In general, those PAHs of high molecular weight (> 3 rings) are associated primarily with fine particles (particles having aerodynamic diameters < 2 μm) in the atmosphere. Because of their small size and their physical-chemical properties, PAH-laden carbonaceous fine particles may be transported through the atmosphere over relatively long distances without being significantly degraded before being deposited. Chemical transformations of PAHs adsorbed onto fine particles are believed to be determined predominantly by reactions with atmospheric oxidants, with photolysis playing a relatively minor role. Recent attention has focused on determining the rate and extent of PAH-transformation and the environmental and health significance of the ultimate products of such reactions.

Depending upon the specific compounds, PAHs in the aqueous and/or particulate phase may enter the aquatic environment either directly or indirectly from both water- and land-based discharges. Surface runoff has been implicated in contributing significant quantities to the PAH loading of aquatic ecosystems. Relatively high levels of certain PAHs have been found in certain locales and have been attributed to identifiable point sources such as municipal effluents and effluents from petroleum refineries and coal conversion plants.

Very little quantitative information is available on the entry of PAHs into the aquatic environment. This is due mainly to the lack of reliable information on the actual fate of PAHs in atmospheric, terrestrial and aquatic environments. For example, the presence of a particular PAH, benzo[a]pyrene (B[a]P), has traditionally been considered an indication of the presence of other PAHs; however, B[a]P has been found to be relatively unstable in oxidizing environments. In addition, the loss of some PAHs, caused by volatilization (i.e. low-molecular-weight PAHs) and/or hemical degradation (i.e. chemically reactive PAHs in the presence of co-existing gaseous pollutants) during atmospheric transport, and the long-term sampling of atmospheric particulate matter have been documented.

As a result of the limited and often imprecise data base, only crude estimates of total PAH input to the aquatic environment can be made. It is estimated that the total B[a]P input from all sources to the aquatic environment is approximately 10^3 $t.a^{-1}$; approximately 10^4 to 10^5 $t.a^{-1}$ total PAHs enter the aquatic environment. Partly because of the different analytical methods used, the term "total PAHs" may represent groups of different PAH compounds. The relative proportion of these totals entering the Canadian aquatic environment is unknown. Atmospheric deposition is considered to be the principal route of entry

of B[a]P, with surface runoff next in importance. Water-based discharges (e.g. petroleum spills, tanker accidents, offshore production, natural seeps) are the predominant routes of entry for total PAHs; atmospheric deposition and surface runoff are the second and third significant routes, respectively. It must be kept in mind that a large fraction of petroleum and associated products contain PAH compounds other than the 4-, 5- and 6-ring PAHs and that B[a]P content in such products is relatively low. Numerous point sources, although not considered significant on a worldwide or national scale, may nevertheless be very important in specific locales.

3.4 FATE IN THE AQUATIC ENVIRONMENT (see Section 3.4)

Abiotic Cycling (see Section 3.4.1)

Because PAHs are generally hydrophobic and have a high affinity for particle surfaces, they are considered to be associated primarily with particulate matter, both suspended and deposited, in the aquatic environment. In special circumstances, some PAHs may be at least partially soluble, such as in water of high humic material content. Polycyclic aromatic hydrocarbons may adsorb to either inorganic or organic surfaces although adsorption to organic materials predominates. A high positive correlation between organic-carbon content and adsorption to suspended particles and bottom sediments has been demonstrated.

Laboratory and field studies have demonstrated that adsorption to particulate matter, with subsequent sedimentation, is the primary removal mechanism of high-molecular-weight PAHs (> 3 rings) from the water column. Photochemical degradation, volatilization and microbial degradation appear to be of minor significance compared with sorption processes. For low-molecular-weight PAHs (< 3 rings), volatilization appears to be the primary removal mechanism in the absence of significant quantities of suspended particles.

Although photooxidation of PAHs in solution is relatively rapid, experimental and field evidence suggest that this process is significantly hindered in the presence of suspended particulate matter. In most natural waters the presence of particles suspended in the water column will confine photolytic activity to the uppermost layers of water.

Biotic Cycling (see Section 3.4.2)

PAHs are accumulated in the aquatic environment in the order sediments > biota >> water. In some cases, tissue levels of PAHs have been found to decrease with increasing distance of the sampled organism from the PAH-emitting source. The uptake of PAHs by biota is not viewed

as a major removal mechanism, but concern has been expressed that PAHs may accumulate to toxic levels, and this has significance for both human and animal health. PAHs are strongly hydrophobic, which favors their accumulation in tissue; uptake of PAHs through water-lipid partitioning occurs across the integument, gills or gut. A general trend seems to be that as PAHs increase in molecular weight, their solubility in water decreases and they accumulate in tissue to a greater extent and for longer periods of time.

A number of factors have been identified which influence the uptake and accumulation of PAHs by aquatic organisms. Studies of fish and birds have shown that lipid content affects the tissue distribution and overall accumulation of PAHs. Uptake of PAHs from food sources appears to be an important route in filter-feeding bivalves, but not in vertebrate fish. In sediments, interstitial water is enriched with the less hydrophobic, low-molecular-weight PAHs, which results in their increased uptake by biota.

Invertebrate and vertebrate aquatic species possess enzyme systems capable of metabolizing PAHs. Molecular oxygen is introduced into the aromatic ring by a NADPH-dependent process, involving the P_{450} network of cytochromes. Further metabolism to produce trans-dihydrodiol, quinone and phenol derivatives, which are more water-soluble than the parent compounds, has been well documented; however, only limited evidence for the formation of conjugated metabolites is available. The highest rates of metabolism have been detected in vertebrate fish and, because of this, biomagnification of PAHs along the entire aquatic food chain does not appear to be a major factor. Metabolism of PAHs has also been detected in polychaete worms, and has been measured at low levels in crustaceans and in molluscs.

Bacteria, fungi and algae also have the enzymatic capability for degrading PAHs. A dioxygenase enzymatic system converts PAHs to cis-dihydrodiols prior to enzymatic cleavage of the aromatic structure. Many PAHs and HACs are resistant to microbial degradation, except in the presence of a co-substrate. Increased degradation rates have been noted in aquatic environments with a history of petroleum pollution. PAH degradation rates may be affected by many environmental factors - redox state, temperature, nutrient content, sediment structure and bioavailability. Structure-activity relationships for degradation of PAHs have also been observed. Naphthalene is most quickly degraded, with degradation rates decreasing for PAHs of increasing molecular weight.

4. EFFECTS ON AQUATIC BIOTA (see Chapter 4.0)

4.1 TOXICOLOGY (see Section 4.1)

Studies with petroleum indicate that naphthalene and phenols, along with mono- and diaromatic compounds (but not the higher-molecular-

weight PAHs), are usually responsible for acute toxicity to aquatic organisms. Naphthalene and several of its methylated derivatives were acutely toxic to a number of marine invertebrates in the range 1-5 $mg.L^{-1}$; larger molecular weight PAHs (> 3 rings) were not acutely toxic within the limits of their solubility. Heterocyclic aromatic hydrocarbons were also tested on invertebrates and found to have LC_{50}s in the low $\mu g.L^{-1}$. Toxicity was found to increase with the addition of each ring to the heterocyclic aromatic structure. Sublethal effects on survival, growth and reproductive capacity have been documented for PAHs and HACs in specific groups of aquatic organisms. In many cases, however, relatively high concentrations of chemicals have been employed.

Structure-activity relationships for mutagenic and carcinogenic activity seem to favor 4-, 5- and 6-ring PAHs rather than smaller or larger compounds. It is believed that PAHs require metabolic activation to exert their carcinogenic effects (epoxides formed in the "bay-region" are extremely reactive), with carcinogenesis being initiated by the binding of electrophilic metabolites to critical cellular constituents. Enzymes other than mixed function oxidases (MFO), which may influence the rate of production or destruction of reactive metabolites, are found in aquatic animals and may play an important role in toxicity.

Short-term mutagenicity assays are valuable in screening for potential mutagenic/carcinogenic compounds, which form reactive electrophiles such as various PAHs. PAHs are found in the environment as complexe mixtures, and the non-mutagenic compounds can be expected to modify the biological responses of any mutagenic/carcinogenic hydrocarbons. Since the bioavailability of PAHs from particulates, water, or sediments is also uncertain, it is premature to suggest that such compounds are definitely involved in aquatic mutagenesis/carcinogenesis. Few laboratory studies on the carcinogenecity of PAHs in aquatic organisms are available. Experiments to date have been carried out with high concentrations of individual compounds; the environmental relevance of such single compound exposures remains to be elucidated.

4.2 ENVIRONMENTAL EFFECTS (see Section 4.2)

Elevated tissue levels ($\mu g.g^{-1}$ range) of PAHs have been documented for animals in coastal and continental waters, but these have not been associated with adverse effects. Most of the information on adverse effects comes from investigations carried out at point-source sites impacted with high levels of petroleum-derived PAHs. Adaptive responses may play an important role in PAH toxicology. Under favorable conditions, the increased growth of hydrocarbon-utilizing bacteria has been associated with the presence of high concentrations of aromatic hydrocarbons. Elevated levels of MFO were found in fish from areas with

a history of hydrocarbon contamination. It is less clear whether the same effect is common in invertebrates.

The frequency of occurrence of a variety of fish tumors and of mutagenic activity in bivalve mollusc extracts appears to bear some relationship to elevated levels of domestic and/or industrial pollution. It has been suggested that these observations could be used as indicators of pollution. To date, PAHs have not been unequivocally identified as the specific causative agents for cancer in any natural population of aquatic animals; instead, the usual situation has been to find traces of PAHs in association with a myriad of other chemicals, although there are some instances of increased tumor frequency where PAHs may have been the dominant pollutant.

RECOMMENDATIONS

The Panel has assessed the present status of scientific information on PAHs as they pertain to the Canadian aquatic environment. Serious gaps in the scientific data base have been noted and research must be increased on the chemical and biological processes related to the presence, fate and distribution of PAHs and PAH mixtures. These data will be essential for trend analysis and the development of predictive models for use in environmental planning and protection. Accordingly, the Panel recommends:

1. A detailed assessment of the methodologies used for the sampling and analysis of PAHs in environmental media should be carried out. The Panel has serious reservations with respect to the adequacy of much of the data base concerning the reported environmental levels of PAHs, especially since factors such as sample contamination and artifact formation are often not considered in a thorough and rigorous manner.

2. Research focusing on the physical-chemical processes that determine the fate of the soluble and particulate forms of PAHs in fresh and marine waters is required. Consideration should be given to modifying factors such as solubilization, chemical degradation, volatilization, photooxidation, sedimentation and sorption phenomena, in particular the determination of surface phenomena associated with plankton.

3. An improved data base on the sources, level, and distribution of PAHs in the Canadian aquatic environment is needed. Particular attention should be directed to representative freshwater and marine environments where land based sources and/or the aerial transport of PAHs are suspected. Consideration should be given to the use of sediment PAH profiles as a means of estimating trends of deposition.

4. Products arising from abiotic transformations of PAHs should be identified and the environmental levels and fate of such compounds should be determined. Attention should also be directed to studies on nitrogen-containing PAHs.

5. The signficance of biosynthesis as a source of PAHs to the aquatic environment should be determined.

6. Given the ability of molluscan and crustacean invertebrates to accumulate PAHs, research must be accelerated on the factors affecting the bioaccumulation of PAHs and PAH mixtures in these species, especially shellfish that have importance in the human food-chain.

7. Toxicological research should be carried out using selected aquatic species exposed to environmentally realistic levels of

PAHs and PAH mixtures in order to quantify the sublethal biological effects of these compounds. The studies should assess any carcinogenic, mutagenic and teratogenic effects, with data being obtained on the various stages in the life history of exposed organisms. This research should lead to the development of toxicological indices with direct application to environmental surveys for assessing the impact of PAHs on aquatic populations.

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1.0 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and related material have been identified in numerous environmental media. The presence of these relatively high-molecular-weight, hydrophobic, organic chemicals has been attributed to both natural and man-made activities. The major concern regarding the presence of PAHs and related chemicals in the environment relates to their genotoxic activity; elevated levels of specific PAHs in the environment and certain aquatic biota are suspected of being related to increased incidences of carcinogenesis and mutagenesis in exposed organisms.

The Subcommittee on Water of the National Research Council of Canada's Associate Committee on Scientific Criteria for Environmental Quality requested that a Panel be assembled to investigate the concern over the presence of PAHs in the aquatic environment. The Panel was charged with the task of critically examining scientific information relating to cause-effect relations between PAHs in the aquatic environment and potential environmental impacts. Where causality could not be established, recommendations for research were made. For this task, the Panel placed special emphasis upon an examination of the sources, mode of transport and transformation and effects in the aquatic environment. The Panel did not address the human safety aspects of the consumption of PAH-contaminated foodstuffs nor the overall human health consequences of exposure to PAHs and related chemicals.

Literature published prior to March 1983 was critically evaluated, with emphasis being placed on the most recent information concerning impacts of PAHs in aquatic habitats. Nomenclature and those physical-chemical properties relevant to environmental situations are summarized in Chapter 2. Chapter 3 presents an examination of the movement of PAHs in the environment and includes a description of the sources of PAHs, their mode of entry into the aquatic environment, and their fate in aquatic ecosystems. Where possible, quantitative information is given. Finally, in Chapter 4, the effects of PAHs in aquatic biota are critically examined, with emphasis on laboratory studies of lethal and sublethal effects, mutagenic and carcinogenic effects, and ecological effects.

2.0 PHYSICAL-CHEMICAL PROPERTIES

2.1 NOMENCLATURE AND STRUCTURE

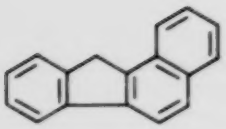
Polycyclic organic matter (POM) is a general term for a diverse range of chemical compounds that include polycyclic (polynuclear) aromatic hydrocarbons (PAHs), aza- and imino-arenes, thia-arenes, carbonyl and dicarbonyl arenes and arene oxides and hydroxides. Compounds having sulfur, nitrogen or oxygen in the aromatic ring are collectively referred to as heterocyclic aromatic compounds (HACs). The number and diversity of compounds within each of these groups dramatically increase when substituents (e.g. alkyl, amino, nitro, etc.) are attached to the rings. Several examples of polycyclic aromatic hydrocarbons and heterocyclic aromatic compounds are illustrated in Figure 2-1.

Classically, any organic compound containing two or more arene structures may be considered in the general classification of polycyclic organic matter. For the purpose of this document, emphasis is placed on those carbon- and hydrogen-containing compounds having three or more fused 5- and 6- membered rings. Information on naphthalene (a two-ring, fused aromatic compound) and its derivatives is used in this document for comparison with PAH compounds having three or more rings. Most of the available scientific information relating to POM deals with PAHs, and hence, emphasis will be placed on this particular class of compounds in this report. However, increasing attention is being focused on heterocyclic aromatic compounds (HACs). The available scientific information on HACs is briefly reviewed in this report, but because of increasing concern regarding the presence of this class of chemicals in the environment, a separate and detailed examination should be conducted.

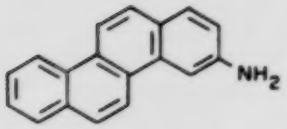
As a general class, PAHs are composed of aromatic structures ranging in molecular weight from 166 to greater than 328. Within this molecular-weight range there exists a multitude of compounds differing in number and position of fused rings and substituents. In the past, PAH nomenclature has suffered from ambiguities due in part to the use of trivial names and of different peripheral numbering systems of the aromatic rings. The currently accepted nomenclature is that adopted by the International Union of Pure and Applied Chemistry (IUPAC 1979) and is discussed in detail in Appendix I. The IUPAC names for some PAHs and HACs, along with some alternate names, abbreviations and molecular formulae, weights and structures, are detailed in Tables I-1 and I-2 of Appendix I.

2.2 PHYSICAL PROPERTIES

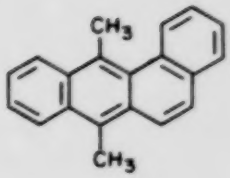
Polycyclic aromatic hydrocarbons and heterocyclic aromatic compounds are usually colored, crystalline solids having high melting



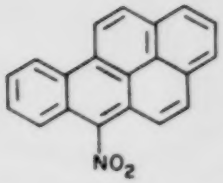
fluoranthene



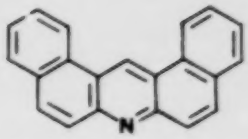
3-aminochrysene



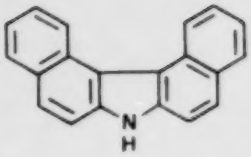
7,12-dimethylbenz[a]-anthracene



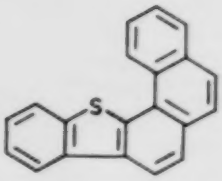
6-nitrobenzo[a]pyrene



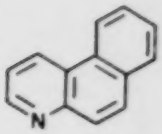
dibenz[a,j]acridine



dibenzo[c,g]carbazole



benzo[b]phenanthro(3,4-d)-thiophene



benzo[f]quinoline

Figure 2-1. Some representative polycyclic aromatic hydrocarbons and heterocyclic aromatic compounds (for a detailed list of compounds see Appendix I).

and boiling points and low vapor pressures and water solubilities (Tables 2-1 and 2-2). Accurate data on the physical properties of many of these compounds are lacking. The melting point has been the only parameter measured consistently; however, the values reported in the literature have often been recorded for either impure compounds or mixtures of isomers.

Because of their relatively low vapor pressures and water solubilities and their affinity for particle surfaces, it is considered that PAHs and HACs are usually associated with suspended particulate matter in both the atmospheric and aquatic environments (see Sections 3.3.1.1 and 3.4.1.1). Although they comprise such a diverse range of organic compounds, some general trends in physical-chemical properties are apparent. As the molecular weight of PAHs increases, their vapor pressure and hence saturation vapor concentration decrease. At elevated temperatures, some PAHs, especially the lower-molecular-weight compounds (i.e. less than 3-4 rings), exist partially in the vapor phase. Loss of material due to volatilization during source sampling at elevated temperatures and during ambient atmospheric sampling for relatively long periods has been reported (see Section 3.3.1.1).

The published values (see Table 2-2) for the aqueous solubilities of PAHs show a wide variation, reflecting in part the different modes of preparation and measurement of PAH solutions. Despite these deficiencies some general trends do exist. As their molecular weight increases, the water solubility of PAHs decreases. Polycyclic aromatic hydrocarbons with a linear arrangement of fused benzene rings are usually less soluble than those having angular or pericondensed structures. Alkyl substitution of the aromatic ring generally decreases water solubility. Temperature has a marked influence on the solubility of PAHs. For example, the water solubility of anthracene increases from 12.7 ± 0.4 $\mu g.L^{-1}$ to 55.7 ± 0.7 $\mu g.L^{-1}$ when the temperature is increased from 5.2°C to 28.7°C (May et al. 1978a). Despite limited data, it appears that PAHs of higher molecular weight (i.e. greater than 3-4 rings) are slightly less soluble in seawater (Eganhouse and Calder 1976; Rossi and Neff 1978; Rossi and Thomas 1981). Values for octanol-water partition coefficients and bioconcentration factors for several PAHs and HACs may be found in Table 3-24.

2.3 CHEMICAL REACTIVITY

Polycyclic aromatic hydrocarbons and HACs undergo chemical reactions characteristic of aromatic organic molecules, including electrophilic substitutions, 1,2- and 1,4-additions and addition-eliminations (Tipson 1964; USNAS 1972). Enhanced reactivities are due, in large part, to the extensive electron delocalization in the intermediate electronic states. The type of reaction that occurs, as well as the rate of reaction, is dependent upon the molecular structure of the substrate in addition to the reagent and milieu. Electron-

Table 2-1. Physical properties of some polycyclic aromatic hydrocarbons.

Compound Name	Molecular Weight	Melting Point °C	Boiling Point °C (101.3 kPa)	Density $g.mL^{-1}$	Vapor Pressure (25°C) kPa	Saturation Vapor Concentration $ng.m^{-3}$ (25°C)	Equilibrium Vapor Concentration ($ng.m^{-3}$) (30°C)	(-10°C)
Fluorene	166.2	116-117 (sublimes)	293-295	1.203_4^0	-	-	-	-
Anthracene	178.2	218 (sublimes)	342	1.25_4^{27}	2.6×10^{-5}	1.9×10^{7}	-	-
Phenanthrene	178.2	100 (sublimes)	340	1.79_4^{25}	9.1×10^{-5}	6.5×10^{7}	-	-
Fluoranthene	202.2	110-111	393	1.252_4^0	-	-	-	-
Pyrene	202.2	156	404	1.271_4^{23}	9.1×10^{-8}	7.4×10^{4}	5.8×10^{2}	1.4×10^{5}
Benzo[a]fluorene	216.3	189-190	-	-	-	-	-	-
Benzo[b]fluorene	216.3	208-209		-	-	-	-	-
Benz[a]anthracene	228.3	159-161 (sublimes)	400	-	1.5×10^{-8}	1.3×10^{3}	3.4	2.8×10^{3}
Benzo[c]phenanthrene	228.3	68	-	-	-	-	-	-
Chrysene	228.3	256 (sublimes)	448	1.274_4^{20}	-	-	-	-
Naphthacene	228.3	341 (sublimes)	-	-	-	-	-	-
Benzo[b]fluoranthene	252.3	167-168	-	-	-	-	-	-
Benzo[j]fluoranthene	252.3	165-166	-	-	-	-	-	-
Benzo[k]fluoranthene	252.3	216-217	480	-	1.3×10^{-11}	1.3×10^{1}	1.3×10^{-2}	3.0×10^{1}
Benzo[a]pyrene	252.3	177-178	475	1.351	7.3×10^{-10}	7.5×10^{1}	1.5×10^{-1}	1.6×10^{2}
Benzo[e]pyrene	252.3	178-179	492	-	7.4×10^{-10}	7.5×10^{1}	1.5×10^{-1}	1.6×10^{2}
Perylene	252.3	273-274	350-340 (sublimes)	1.35	-	-	-	-
Benzo[ghi]perylene	276.3	277	-	-	1.3×10^{-11}	1.5	1.8×10^{-3}	3.4
Dibenzo[def,mno]chrysene	276.3	259	-	-	-	-	-	-
Indeno[1,2,3-cd]pyrene	276.3	163-164	-	-	-	-	-	-
Dibenzo[a,def]chrysene	278.4	278	-	-	-	-	-	-
Dibenzo[b,def]chrysene	278.4	306	-	-	-	-	-	-
Dibenzo[def,p]chrysene	278.4	223	-	-	-	-	-	-
Naphtho[1,2,3,4-def]chrysene	278.4	238	-	-	-	-	-	-
Dibenzo[ghi,pqr]chrysene	300.4	438-440	525	1.377	2.0×10^{-13}	2.0×10^{-2}	1.8×10^{-6}	5.8×10^{-2}
Naphtho[8,1,2-cde]naphthacene	302.4	272	-	-	-	-	-	-

donating substituents such as alkyl and alkoxy groups generally increase the rate of nucleophilic reaction. Although most experiments on chemical reactivity have been conducted in non-aqueous solvents, some work has been carried out in the vapor, particulate and aqueous phases.

In the presence of light and oxygen, PAHs and HACs readily undergo photooxidation. Polycyclic aromatic hydrocarbons and HACs readily absorb radiation at wavelengths ranging from 200 to 400 nm. Absorption of incident radiation results in activation of the ground state molecule to an excited singlet state which, in the absence of fluorescence, may react with a second ground state molecule to produce a photodimer or undergo a transition to an excited triplet state. Reaction of the excited triplet state with ground-state molecular oxygen produces excited-singlet molecular oxygen which in turn reacts with a ground-state PAH or HAC molecule to yield oxygenated products (USNAS 1972). The primary intermediates of photooxidation are endoperoxides, which, upon further photolysis or thermal degradation, undergo dealkylation and ring cleavage. When, for steric reasons, endoperoxide intermediates cannot be formed, quinones are produced.

One-electron oxidations occur readily, the primary intermediates being radical cations. Being unstable, radical cations rapidly react with water or some other nucleophile, such as a second PAH molecule, and with oxygen to produce diols, quinones, aldehydes or dimers (USNAS 1972).

Polycyclic aromatic hydrocarbons and azaarenes are susceptible to attack by ozone, although azaarenes are generally less reactive. Ozone-PAH reactions usually occur via 1,2- or 1,4-additions as well as substitution and result in the formation of diacids and quinones. Alkylated PAHs may also undergo side-chain oxidation. Other oxidants include hydroxy-, hydroperoxy-, alkyl- and arylperoxy-radicals and peroxides. Nitrogen and sulfur oxides, as well as nitric and sulfuric acids, readily react with PAHs via substitution reactions to yield the corresponding nitro derivatives and sulfinic or sulfonic acids. Nitration (Pitts 1979) and sulfonation (Tebbins et al. 1966; Jaeger and Rokovic 1974) of PAHs have been demonstrated. A review of the formation of nitro derivatives of PAHs may be found in Neilson (1982).

2.4 DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN ENVIRONMENTAL SAMPLES

The concentrations of PAHs in environmental samples are generally very low and fluctuate widely, both temporally and spatially. Many analytical techniques have been developed for the analysis of PAHs in air, water, sediment and biological samples; such techniques range from relatively simple and rapid semi-quantitative methods to very elaborate and expensive procedures for full quantitative analyses.

Table 2-2. Solubility of some polycyclic aromatic hydrocarbons in water (25°C).

Compound Name	Solubility $\mu g.L^{-1}$	Reference
Fluorene	800[α]	Rossi and Neff (1978)
Anthracene	30	Schwarz and Wasik (1976)
	41	Schwarz (1977)
	41.3	Leinonen and Mackay (1973)
	44.3	May et al. (1978a)
	44.6	DiCorcia and Giabbai (1978)
	73	MacKay and Shiu (1977)
	75 (29°C)	Davis et al. (1942)
	75	Pierotti et al. (1959)
	75	Wauchope and Getzen (1972)
	57	Whitehouse and Cook (1982)
2-Methylanthracene	21.3	May et al. (1978b)
	24.2	May et al. (1978a)
	28.8	Whitehouse and Cook (1982)
Phenanthrene	994	Andrews and Keefer (1949)
	1002	May et al. (1978b)
	1070	Eganhouse and Calder (1976)
	1151	Schwarz (1977)
	1180	Wauchope and Getzen (1972)
	1290	MacKay and Shiu (1977)
	1600 (29°C)	Davis et al. (1942)
	1600	Klevens (1950)
	600[α]	Rossi and Neff (1978)
	710[β]	Eganhouse and Calder (1976)
	1782	Whitehouse and Cook (1982)
1-Methylphenanthrene	269	May et al. (1978b)
	300[α]	Rossi and Neff (1978)
4,5-Dimethylphenanthrene	1100	Davis et al. (1942)
Fluoranthene	206	May et al. (1978b)
	236	Schwarz and Wasik (1976)
	240	Andrews and Keefer (1949)
	240 (29°C)	Davis et al. (1942)
	260	MacKay and Shiu (1977)
	265	Klevens (1950)
	265	Wauchope and Getzen (1972)
	1[illegible][α]	Rossi and Neff (1978)
Pyrene	129	Schwarz (1977)
	132	May et al. (1978b)
	135	MacKay and Shiu (1977)
	165 (29°C)	Davis et al. (1942)
	171	Schwarz and Wasik (1976)
	175	Klevens (1950)
	90[β]	Rossi and Thomas (1981)

Table 2-2. (Cont'd).

Compound Name	Solubility $\mu g.L^{-1}$	Reference
Benzo[d]phenanthrene	38 (29°C)	Davis et al. (1942)
	43	Klevens (1950)
Chrysene	1.5 (29°C)	Davis et al. (1942)
	1.8	May et al. (1978b)
	2	MacKay and Shiu (1977)
	6	Klevens (1950)
	6	Pierotti et al. (1959)
	1.9	Whitehouse and Cook (1982)
Naphthacene	1.0 (29°C)	Davis et al. (1942)
	≈1.5	Klevens (1950)
Benz[a]anthracene	9.4	May et al. (1978b)
	10	Klevens (1950)
	10	Pierotti et al. (1959)
	11 (29°C)	Davis et al. 1942
	14	MacKay and Shiu (1977)
	11.4	Whitehouse and Cook (1982)
10-Methylbenz[a]anthracene	55 (29°C)	Davis et al. (1942)
10-Ethylbenz[a]anthracene	45 (29°C)	Davis et al. (1942)
10-Butylbenz[c]anthracene	8 (29°C)	Davis et al. (1942)
10-Amylbenz[a]anthracene	0.8 (29°C)	Davis et al. (1942)
9,10-Dimethylbenz[a]anthracene	43 (29°C)	Davis et al. (1942)
Benzo[a]pyrene	0.2	Lu et al. (1977)
	0.5	Eisenbrand (1971)
	4 (29°C)	Davis et al. (1942)
	6.1	Weil-Malherbe (1946)
5-Methylbenzo[a]pyrene	≈0.8 (29°C)	Davis et al. (1942)
Benzo[e]pyrene	≈4	Schwarz and Wasik (1976)
Perylene	<0.5 (29°C)	Davis et al. (1942)
	0.4	Whitehouse and Cook (1982)
Dibenz[a,c]anthracene	0.5 (29°C)	Davis et al. (1942)
	≈0.6	Klevens (1950)
Picene(Benzo[b]napthacene)	2.5 (29°C)	Davis et al. (1942)

α 32 °/oo salinity, 22 ± 2°C.

β 35 °/oo salinity, 25 ± 0.5°C.

Because PAHs are usually in low concentrations in environmental samples and are associated with a number of similar and often interfering chemicals, proper precautions have not always been taken during the sampling and analysis of such compounds. Concern has been raised with respect to the accuracy and reliability of numerous methods of analysis as well as their representativeness and applicability. Serious reservations have been expressed in the literature regarding the adequacy of the data base with respect to environmental levels of PAHs, especially when factors such as sample contamination and artifact formation have not been properly considered. A detailed assessment of the methodologies used for the sampling and analysis of PAHs is beyond the scope of this document. The Panel recommends that a comprehensive, separate report examining this topic should be prepared. For that reason, this section will be limited to a summary of some review articles which reflect the trend employed for the analysis of PAHs during the last decade.

Reviews of the determination of PAHs in water have been prepared by Harrison et al. (1975) and Futoma et al. (1981). Most analytical laboratories use single or multiple-step extractions of water samples either with benzene, cyclohexane, n-hexane or n-pentane (Acheson et al. 1976). The extracts are concentrated and analyzed by gas chromatography (GC), thin-layer chromatography (TLC) and liquid chromatography (HPLC) or by gas chromatography/mass spectrometry (GC/MS).

Environmental samples have usually been collected by grab sampling techniques (Goulden 1978). The initial sample size may vary from 10 g to 1 kg. Samples include fish, birds, oysters, eggs, and mammals that have been hand collected or netted. In some cases, dead specimens are analyzed in relation to direct environmental contaminants (e.g. oil spills).

The ultimate goal of analytical methodologies employed for PAHs is the identification, determination and confirmation of a single component. However, because of their relative chemical similarity, PAH compounds mixed with other organic contaminants are rather difficult to separate, identify and quantify. One of the most effective means of achieving the separation of a complex mixture is chromatography. Thin-layer chromatography for the separation of PAHs has been reviewed by Van Langermeersch (1968), Halot (1970), Schaad (1970), and Herod and James (1978). Liquid chromatography and high-pressure liquid chromatography (HPLC) are the most recent techniques to be applied to the separation of PAHs (Sorrell et al. 1977).

The present state of the art in open tubular column (WCOT) chromatography for PAH and HAC compounds was reviewed by Lee and Wright (1980). The superiority of WCOT column GC in resolving components in complex mixtures of PAHs also extends the limits of detection when sharp, narrow peaks are eluting from the column. The tandem of WCOT

column GC with the use of mass spectrometry may afford a sensitive but expensive means of determining the identity and specificity, besides improving the sensitivity when selected ion monitoring is employed (Lee et al. 1979b). Photoluminescence analysis has become well-established as a selective and sensitive method for PAH analysis and it has been found to be competitive with mass spectrometric detection (Brown et al. 1978).

An analytical method must provide reliable data for PAH analysis to ensure the validation of collaborative studies for isomers, photodegradation and bioalteration products. However, the majority of methods reviewed have been inadequately validated for matrices of animal origin and (to a lesser extent) for plant tissues or associated matrices such as water and soil.

3.0 ENVIRONMENTAL DYNAMICS

Polycyclic aromatic hydrocarbons and associated material may enter the aquatic environment via a number of different routes including 1) the release of material to the atmosphere, primarily through combustion, followed eventually by deposition in the aquatic environment, either directly or by deposition on land with subsequent surface runoff or transport to groundwater, and 2) the release of material directly to the aquatic environment, or indirectly through land disposal, without first being transported through the atmosphere. These two general routes of entry are responsible for both the background levels of many PAHs recorded at sites removed from identifiable sources and the elevated levels associated with site-specific releases. In order to elucidate the fate of PAHs and associated material in the aquatic environment and to determine the environmental significance of the presence of such compounds, it is necessary to examine their formation, sources, transport and transformation.

3.1 FORMATION

It has traditionally been assumed that the majority of PAHs present in the environment have been derived from the inefficient combustion of organic matter. In the context of this document, combustion refers to the rapid chemical combination of oxygen with the combustible materials of a fuel. Combustion is often referred to as any chemical process accompanied by the evolution of heat and light. Recent refinements in analytical methodology have revealed complex PAH mixtures in environmental samples that cannot be explained solely by PAH formation via combustion. The presence of PAHs in the environment is now considered to be due to combustion, diagenesis and biosynthesis.

3.1.1 COMBUSTION

There is no one general pathway for the formation of PAHs and HACs during combustion; instead, formation involves multiple reaction pathways consisting of various intermediates and final products and is dependent upon the composition of organic precursors, the reaction temperatures, the duration of exposure to combustion conditions, and other variables.

Reducing atmospheres, which can exist within a burning flame or in a combustion chamber, are favorable environments for the thermal formation of PAHs. Two mechanisms for the high-temperature formation of PAHs have been proposed: 1) the CH-radical mechanism and 2) the diene synthesis mechanism.

At elevated temperatures (>450°C) in a reducing atmosphere, complex organic molecules are partially cracked to smaller, unstable

intermediates, including free radicals (i.e. pyrolysis). In the context of this document, pyrolysis refers to the chemical decomposition or other chemical change brought about by the action of heat. These fragments may then recombine to form relatively stable aromatic hydrocarbons and heterocyclic compounds (i.e. pyrosynthesis). Ethylene, acetylene and 1,3-butadiene intermediates undergo polymerization reactions followed by cyclization and dehydrogenation to form simple aromatic structures (Badger 1962; Badger et al. 1960, 1964, 1965, 1966). Once formed, these relatively simple PAHs undergo further pyrosynthetic processes to form more complex PAHs.

Fragmentation to C_1-C_3-radicals is not always necessary for PAH synthesis. Pyrolysis of benzene yields naphthalenes and higher-molecular-weight PAHs via a benzyne intermediate (Hoffman and Wynder 1977). Terpenes, upon pyrolysis, yield isoprenoid and other diene intermediates which may form PAHs via a Diels-Alder addition (i.e. diene synthesis).

Numerous organic compounds have been tested for their ability to generate PAHs under pyrolytic conditions. Carbohydrates are relatively poor PAH precursors compared with lipids (Schmeltz and Hoffman 1976). Although chain length has little effect on the total yield of PAHs formed pyrolytically, increased chain branching and unsaturation lead to increased yield of PAHs under identical combustion conditions. The combustion of fuels containing aliphatic hydrocarbons results in low yields of PAHs compared with combustion of regular gasoline having a 30% aromatic hydrocarbon content (Brunnemann and Hoffman 1976). Cyanonaphthalenes and cyanoacenaphthalenes have been identified as the major nitrogen-containing products generated from the combustion of aromatic hydrocarbon fuels doped with pyridine (Dubay and Hites 1979).

Consistent with the diene synthesis mechanism for PAH-formation, Brunnemann and Hoffmann (1976) and Hoffmann and Wynder (1977) found that compounds having a steroid configuration were good precursors for chrysenes and benzopyrenes. The reaction of isoprenes, indenes and other dienes with acenaphthalenes under pyrolytic conditions yielded fluoranthenes.

Temperature plays a significant role in the synthesis of PAHs. Badger et al. (1964) found that the maximal yields of benzo[a]pyrene (B[a]P) and benzo[b]fluoranthene (B[b]F) occurred above 650°C during pyrosynthesis. They suggested that significant differences may exist in the temperature at which individual PAH compounds are formed with maximal yields. The relative abundance and molecular weight distribution of alkylated PAHs are also dependent upon combustion temperatures. At very high temperatures (2000°C) the products consist of relatively simple mixtures of unalkylated PAHs with a small amount of alkylated PAHs (Blumer and Youngblood 1975; Herlan 1978). As the temperature decreases, the extent of PAH alkylation increases. At

intermediate temperatures (400-800°C) substantial quantities of alkylated PAHs may be formed. Combustion at these intermediate temperatures would permit the survival of some alkylated products but would eliminate extended alkyl chains by thermal cracking (Blumer 1975).

The presence of complex mixtures of PAHs, HACs and their alkyl homologs in soils and recent sediments has been well-established (Blumer and Youngblood 1975; Hites and Biemann 1975; Wakeham and Farrington 1980). This fraction was found to consist of relatively large quantities of unalkylated compounds compared with alkyl homologs. Blumer and Youngblood (1975) observed a nearly twofold decrease in the concentration of alkylated compounds with each additional carbon atom attached to the alkyl chain. The molecular-weight distribution of the alkylated PAH fraction was markedly different from that of ancient sediments and crude oils where PAH alkylation is much more extensive. Unsubstituted azaarenes containing 3 to 5 aromatic rings were found in higher concentrations than the more numerous alkylated homologs in recent lake sediments (Wakeham and Farrington 1980). Azaarenes in ancient sediments had a much more complex composition, with alkylated azaarenes in much higher concentration than unsubstituted compounds.

Results such as those reported above led Blumer and Youngblood (1975) to speculate that open burning (such as forest fires) with subsequent atmospheric transport and deposition resulted in the observed alkyl PAH mixtures. Hites *et al.* (1977) dismissed these sources as a major input of PAHs to the aquatic environment since environmental mechanisms (e.g. differential solubility, affinity to particle surfaces, chemical reactivity, biodegradation), which could modify the homolog distribution of PAHs, were not taken into account (Hase and Hites 1976). Interpretation of the results from analysis of sediment cores led Hites *et al.* (1977) to state that PAH compounds present in soil and recent aquatic sediments had an anthropogenic origin. However, the results of sediment surveys in Narragansett Bay, Rhode Island, suggested to Lake *et al.* (1979) that a combination of inputs of PAHs from combustion and petroleum processes, rather than solubility alteration of PAH mixtures originating from a single source, accounted for the observed distribution of alkylated and unalkylated PAHs.

Other factors that may affect the molecular-weight distribution and degree of alkyl homolog complexity of PAH mixtures during combustion have not been adequately studied. For example, Blumer (1975) speculated that extended reaction times at high temperatures may yield a higher proportion of unalkylated PAHs as well as diminish the content of less stable PAHs. The effects of radical scavengers on rate and extent of PAH formation have not been adequately examined.

3.1.2 DIAGENESIS

Low temperatures (<150°C) favor the formation of alkylated PAHs (Youngblood and Blumer 1975). Slow transformation of PAH

precursors leads to extensive alkyl and cycloalkyl substitution and to the low relative abundance of unalkylated compounds in each PAH homologous series (Blumer 1975). Fossil fuels can be a rich source of very complex PAH mixtures. Crude oils and shale oils have a predominance of alkylated PAHs. A similar high ratio of alkylated to unalkylated PAHs is found in residual oils (e.g. Bunker C oil) and asphalts (see Section 3.2.2.2.1).

The molecular weight and substitution patterns of these mixtures are influenced by the source of PAH precursors as well as by depositional and preservational histories (Aizenshtat 1973). A wide variety of pigments of biosynthetic origin have been identified in the environment (Thompson 1971). Certain polyhydroxyquinone pigments may undergo dehydrogenation, dehydroxylation and aromatization under reductive conditions in anoxic sediments to yield certain PAH compounds (Maxwell et al. 1971). Precursors with anthraquinone structures have been shown to form PAH compounds having anthracene- and perylene-type structures. In addition, chrysene-type PAH compounds have been formed during the diagenesis of steroids and terpenoid precursors. In an investigation of the sources and fate of PAHs in recent lake sediments, Wakeham et al. (1980a) found a wide range of aromatic compounds that could not be attributed solely to anthropogenic sources. These compounds were identified as perylene, phenanthrene homologs, retene and pinanthrene, and tetra- and pentacyclic PAHs derived from pentacyclic triterpenes. Molecular structure and depth profiles indicated to the authors that these compounds might have been formed in sediments by the transformation of biogenic precursors. Once formed, PAHs may remain relatively unchanged in undisturbed anoxic sediments.

3.1.3 BIOSYNTHESIS

Certain bacteria, fungi, higher plants and some animals are capable of synthesizing a wide variety of polycyclic quinone pigments (Thompson 1971), which may be converted into certain PAHs during diagenesis (see Section 3.1.2); however, controversy still surrounds the complete biosynthesis of PAHs. Evidence both for and against the complete biosynthesis of selected PAHs has been well documented (Neff 1979). In many cases of reported PAH biosynthesis, the possibility of exogeneous contamination was not adequately considered. Biosynthesis of certain PAHs by some bacterial cultures may, however, occur to a limited extent under specific environmental conditions. It is expected that the resulting PAH mixtures would be relatively simple and would remain relatively close to the site of formation. Formation by soil microorganisms followed by surface runoff could be one route of PAH entry into the aquatic environment. Input to the global PAH budget via biosynthesis is not considered to be important but may be significant in localized situations (Suess 1976).

3.2 SOURCES

A multitude of sources have been identified from which PAHs and related materials can be released to the aquatic environment. Since the advent of modern analytical techniques, the readily available information on sources and identification in various environmental media has dramatically increased. In addition, many excellent reviews on the sources of atmospheric and waterborne PAHs have been prepared (cf. Andelman and Suess 1970; Andelman and Snodgrass 1974; Harrison et al. 1975; Radding et al. 1976; Neff 1979; Santodonato et al. 1981). The intent of this document is not to duplicate such efforts, but to assess the relevant scientific literature in an attempt to quantify the routes of exposure of this material to aquatic organisms, and to put into perspective their significance in the aquatic environment.

3.2.1 ATMOSPHERIC SOURCES

In general, emissions of PAHs and HACs to the atmospheric environment result from either the inefficient combustion or pyrolysis of organic materials, or from the vaporization and/or aerosol formation of materials that contain these compounds. Once emitted, this material may be dispersed and eventually deposited. Because considerable attention has been focused on the emissions of such material to the atmosphere, numerous excellent reviews on the subject are available (cf. Junk and Ford 1980; Shabad 1980). A brief description of sources and emissions is presented below. Emission factors and rates of emission to the atmosphere are detailed later (see Section 3.2.1.6).

Atmospheric emissions of PAHs and HACs may be grouped into several general categories, including emissions from industrial processes, fuel combustion (stationary sources), transportation, solid-waste incineration and miscellaneous sources such as forest fires, agricultural burning, cigarette smoking, etc. The general designation of sources of pollutants to the atmosphere may be found in EPS (1981).

3.2.1.1 Industrial Processes

The production of coke results in the atmospheric release of significant quantities of PAHs (cf. USEPA 1978a; Eisenhut et al. 1982). Over 60 different PAH compounds have been identified and measured in various unit operations in the production process (Lao et al. 1975; York Research Corporation 1978). Most of these emissions occur through gas leakage during the operational steps. A review of the emissions of PAHs from coke ovens may be found in a report on the designation of coke-oven emissions in Ontario (Ontario Ministry of Labour 1982). The catalytic cracking process is a major petroleum-industry source of atmospheric PAH emissions. In this process, the cracking of crude oil takes place in the presence of a catalyst that is deactivated through the deposition

of carbon and/or coke on its surface. The catalyst is regenerated through the combustion of the carbon/coke and PAHs are formed during this process. Aluminum reduction employs large quantities of carbon paste electrodes that will release PAHs during use (Cretney et al. 1982). Emissions of PAHs from other industrial processes such as charcoal and carbon black manufacture are reviewed by Uthe (1979).

3.2.1.2 Fuel Combustion (Stationary Sources)

During heat and power generation, PAHs are formed from the burning of wood and fossil fuels. Although emitted from a vast number of diverse stationary sources, the amounts released are somewhat dependent on the relative efficiency of the combustion process, with lower emissions occurring for the more efficient operations. For example, Natusch (1978) found that total PAH emissions from fossil-fueled power plants were relatively low, as long as efficient combustion conditions were maintained. The residential combustion of fuelwood in fireplaces and woodstoves constitutes a significant source of atmospheric PAHs in certain locales (Peters et al. 1981; Murphy et al. 1982).

3.2.1.3 Transportation

Internal combustion engines may release PAHs to the atmosphere. Nitro-derivatives of PAHs have been identified in particulate matter collected from the exhaust of automobiles. For example, Gibson (1982) identified 1- and 6-nitropyrene in the exhaust of cars using leaded and unleaded gasoline and diesel fuel. The amount of PAHs and HACs emitted is affected in part by the type of engine, combustion conditions, and emission control devices (Mohr 1978; Nielson 1979; Grimmer 1981). The use of efficient emission control systems, when in proper working order, may significantly reduce PAH emissions from recently manufactured automobiles (cf. Williams and Swarin 1979).

Appreciable emissions of PAHs and HACs may occur from overloading or poor maintenance of diesel engines and the lack of emission controls (Spindt 1978). Yu and Hites (1981) identified several alkylated phenanthrenes, fluorenes and fluorenones - in addition to other PAHs and one nitropyrene compound - in diesel engine particulate matter. Two-cycle engines, which operate on an oil/gas mixture, produce elevated levels of B[a]P relative to 4-cycle engines (Guerin 1978). Because carbon black, which is known to contain a variety of PAHs (Gold 1975), is used as a reinforcing agent for synthetic rubber, significant quantities of PAHs may be emitted to the atmosphere through tire wear.

3.2.1.4 Solid Waste Incineration

Although there is little information available, solid waste incinerators that operate inefficiently, or in the absence of adequate

pollution control devices, may contribute significant amounts of PAHs to the atmosphere. Such emissions vary as a function of the material incinerated and the operating conditions. In their examination of the fly ash collected from an electrostatic precipitator of a municipal incinerator, Eiceman et al. (1981) and Clement and Karasek (1982) identified several PAHs. The compounds found in highest concentration were anthracene and pyrene; B[k]F and benzopyrene (isomer unspecified) were found in relatively low concentrations. In general, the differences in PAH content of collected fly ash paralleled the differences in content of estimated total organic compounds.

3.2.1.5 Miscellaneous

Non-industrial sources may play significant roles in the release of PAHs and HACs to the environment. For example, forest fires and other open burning of organic matter were considered to be the most important sources of PAH emissions in Ontario in 1976 (MOE 1979). The open burning of grass, leaves, bark and branches is also considered to emit large quantities of PAHs (McMahon and Tsoukalas 1978).

3.2.1.6 Estimated Emissions to the Atmosphere

Much effort has been devoted to developing estimates of the release of PAHs and HACs to the atmospheric environment from combustion processes. However, the current data base is still insufficient for the complete quantification of emissions from all sources.

It is very difficult to quantify the emission rates of PAHs and HACs to the atmosphere and their subsequent input to the aquatic environment. Several limiting factors affect the development of quantitative emissions estimates. Very little information is available on the emission of PAHs and HACs from Canadian sources. Because of its carcinogenic potential, B[a]P has been the most intensively studied PAH. Its presence has traditionally been considered an indication of the presence of other PAHs (cf. Suess 1976; Hites 1981). However, B[a]P may constitute only 1-20% of the total PAHs present (USNAS 1972) and no consistent correlation has yet been found between it and other PAHs and HACs. Some work has been done on establishing PAH profiles using several PAHs instead of B[a]P alone as indicators (cf. Grimmer 1981). There is also evidence to indicate that B[a]P is one of the more reactive PAHs in environmental samples, and hence, if used as an indicator, it may underestimate PAH emissions (see Section 3.3.1.1). As indicated previously (see Section 2.4), the methodologies for sampling, cleanup and analysis are not always detailed by individual investigators, and consequently, intercomparisons of results are not always possible. Emissions of PAH compounds may vary over several orders of magnitude for a particular source, depending upon the age and condition of equipment, combustion of feed material, operating

Table 3-1. Emission factors for benzo[a]pyrene and total PAHs. Emission factors are in units of $\mu g.kg^{-1}$ unless otherwise indicated (updated from Ramdahl 1981).

Source type	Benzo[a]pyrene Typical	Benzo[a]pyrene Range	Total PAHs[a] Typical	Total PAHs[a] Range	Reference
INDUSTRIAL PROCESSES					
Coke production			15 000		Trenholm and Beck (1978)
	2100				MOE (1979)
	200				Eisenhut et al. (1982)
Petroleum catalytic cracking					
No central CO heat broiler	.410	.031-.710	28	14-3200	Hangebrauck et al. (1967) Energy and Environmental Analysis Inc. (1978); Oil and Gas Journal (1977)
Aluminum smelting	15 000	10 000-38 000	470 000	400 000-1 300 000	Bjorseth (1982)
Anode baking	66		50 000		
Iron and steel sintering	17	0.6-1100	340		Energy and Environmental Analysis Inc. (1978); St. Louis (1977)
Ferrous foundries			7 700		Vena (1982)
Ferro-alloy industry			10 000		Berglind and Gjessing (1980)
Iron works			60 000		Berglind and Gjessing (1980)
Carbon black production			300	220-490	Energy and Environmental Analysis Inc. (1978); Vandegrift et al. (1970); Vena (1982)
Asphalt production					
Air blowing	1	0.2-750	50	2.8-4100	Hangebrauck et al. (1967)
Shingle saturators	.001	.08-400	5	1-50	Energy and Environmental Analysis (1978)
FUEL COMBUSTION (STATIONARY SOURCES)					
Utilities					
Pulverized coal-fired power plants	1.6	1.1-2.7	19	0.5-32	Hangebrauck et al. (1967) Energy and Environmental Analysis Inc. (1978); Supernant (1976)
Industrial					
Coal-fired boilers	0.9		41		Hangebrauck et al. (1967)
Oil-fired boilers	1.1		23	5.3-100	Energy and Environmental Analysis Inc. (1978); Supernant et al. (1976)
Commercial					
Oil-fired boilers	40		820		Hangebrauck et al. (1967)
Gas-fired intermediate boilers	10			490-1100	Energy and Environmental Analysis Inc. (1978)

Table 3-1. (Cont'd)

Source type	Benzo[a]pyrene Typical	Benzo[a]pyrene Range	Total PAH Typical	Total PAH Range	Reference
Residential					
Fuelwood					
Fireplace (seasoned oak)			25 000		Peters et al. (1981)
(green pine)			36 000		"
Baffled woodstove (seasoned oak)			21 000		"
(green pine)			37 000		"
Non-baffled woodstove					
(seasoned oak)			19 000		"
(green pine)			32 000		"
Coal furnace	1500		60 000	1000-1 200 000	Hangebrauck et al. (1967) DeAngelis and Reznik (1979)
Oil furnance					
30 kw	2.2	2.0-4.4	10 000	0.9-21.6	Herlan (1978)
7.5 kw				900-21 600	
TRANSPORTATION					
Gasoline-powered cars					
No catalyst	1.7 μg.km^{-1}	0.18-3.3 μg.km^{-1}			Williams and Swarin (1979)
	3.2 μg.km^{-1} (cold start)				"
	0.5 μg.km^{-1} (not start)				"
Catalyst	0.04 μg.km^{-1}	0.02-0.07 μg.km^{-1}			"
Diesel-powered cars	1.7 μg.km^{-1}				"
	2.4 μg.km^{-1} (cold start)				"
	1.1 μg.km^{-1} (not start)				"
SOLID WASTE INCINERATION					
Municipal refuse (open burning)			1400		Hangebrauck et al. (1967) Energy and Environmental Analysis Inc. (1978)
Automobile tires (open burning)			240 000		Hangebrauck et al. (1967) Energy and Environmental Analysis Inc. (1978)
MISCELLANEOUS					
Burning of landscape refuse	150				USNAS (1972)
Burning of grass clippings, leaves and branches	346				USNAS (1972)
Hardwood leaf burning		100-800			Jones (1975)
Forest fires (backing)		238-2454			McMahon and Tsoukalas (1978)
(heading)		38-97			McMahon and Tsoukalas (1978)
Cigarette smoking	3-4 μg/100 cigarettes				Hoffman and Wynder (1976)

[a] The individual compounds that constitute the "Total PAHs" fraction are rarely listed in the available literature. The designation "Total PAHs" usually reflects the analytical procedures used or, in some cases, the amount of a particular crude fraction or the sum of PAH compounds identified by a particular technique. Often the amount of B[a]P is used to estimate the amount of "total PAH" by assuming a particular ratio of B[a]P to "total PAHs" in the sample being analyzed.

conditions, and pollution control devices. In general, much of the available information lacks supporting data on sampling location in relation to other potential sources, instrumental specifications, and meteorological conditions; therefore, much of this information is of limited use in attempts to develop emission estimates.

Rates of emission are usually calculated from emission factors, defined as statistical averages of the rates at which a contaminant is released to the atmosphere as a result of some activity (e.g. combustion, industrial production), divided by the level of that activity (EPS 1981). There are a number of inherent problems encountered when calculating emission rates from emission factors. For example, the same emission factor may not apply to all emitters for a particular source at all times. In addition, the relative proportions of PAHs and HACs existing as vapors and as particulate matter will vary depending upon the sampling location within an emission source (Natusch 1978). If only particulate matter is sampled, a serious underestimation of the emission factor could occur (cf. Stenberg 1981). Schure and Natusch (1982) predicted that most of the PAHs will be adsorbed on carbonaceous particulate matter; this carbonaceous material cannot be efficiently extracted since PAHs are tenaciously held by this substrate. Hence, existing emission factors may underestimate PAH emission rates.

In spite of the above difficulties, a number of emission factors and emission rates have been developed for various source types. Emission factors for various sources (e.g. industrial processes, fuel combustion - stationary sources, transportation, solid waste incineration, etc.) are presented in Table 3-1. It is evident that some emission factors may vary by several orders of magnitude for the same source.

The most comprehensive data base on PAH emissions was first developed in 1967 (Hangebrauck et al. 1967) and has been updated and refined (cf. USNAS 1972; Suess 1976; USEPA 1978b; Peters et al. 1981; Ramdahl 1981). Numerous changes have occurred in the designations of source categories in the past few years.

Reliable information on the existence of a background level of PAHs is lacking but it is generally considered that the PAHs identified in environmental samples collected in remote areas originate from both natural and anthropogenic sources. The concentration of PAHs, if expressed as B[a]P, is approximately 10-20 $\mu g.kg^{-1}$ dry organic matter (WHO 1970). The concentration of B[a]P measured in unpolluted non-urban air varies from 0.1 to 0.5 $\mu g.m^{-3}$ (USNAS 1972).

Active volcanoes are considered to be one natural source of PAHs in the environment. Il'nitskii (1980) detected B[a]P in volcanic ash, lava and in samples of soil, vegetation and hot water collected at active volcanoes. Emissions from such sources are expected to be relatively minor in comparison to the total amount of PAHs entering the

biosphere (Suess 1976); however, the identification of B[a]P in permafrost up to 10 000 years old led Il'nitsky et al. (1979a) to observe that the existence of a natural background of PAHs in early historical ages could be attributable to volcanic activity. Sources such as forest fires and other open burning were not considered.

The global B[a]P atmospheric emissions from man-made sources between the period 1966-1969 are estimated to be 5000 $t.a^{-1}$ (tonnes per annum) (Suess 1976), including about 1300 $t.a^{-1}$ emitted in the United States (USNAS 1972) (Table 3-2). Depending upon the emission factors used and the sources considered, emissions of total PAHs in the United States have been estimated to differ from 8400 to 11 000 $t.a^{-1}$ (Tables 3-3 and 3-4). In the past few years, the ranking of sources which are considered to emit significant amounts of PAHs has changed dramatically. For example, Suess (1976) considered fuel combustion in utilities and industrial facilities to be the single largest source of PAHs, followed by coal-refuse fires and coke production (Table 3-2). However, Peters et al. (1981) considered residential combustion to be the major emission source in the United States, followed by open burning (i.e. agricultural, forest), transportation (gasoline-powered automobiles) and coke production (Table 3-4). Using similar data, Ramdahl (1981) considered residential combustion (fuelwood), aluminum smelting and forest fires to be the three largest atmospheric sources of PAHs in the United States (Table 3-3).

There is currently no nationwide PAH emission inventory for Canada. The Ontario Ministry of the Environment, using emission factors developed by USEPA (1978b), calculated estimated B[a]P emissions from various known and potential sources in the province of Ontario (MOE 1979). They identified forest fires and open burning as the most significant contributors to atmospheric loading. Using a similar statistical analogy and B[a]P emission factors, a preliminary inventory was prepared for the possible PAH emissions in Canada (see Table 3-5). Total emissions are estimated at 19 to 22 $t.a^{-1}$ for B[a]P, with coke production, aluminum reduction and petroleum cracking being the three most significant industrial processes emitting B[a]P. Emission rates for forest fires, open burning and residential and industrial fuelwood combustion are not yet available for Canada. In addition, information on estimated emissions from recreational vehicles such as motorboats, snowmobiles, etc. is not available. The PAH emissions from marine vessels have not been studied and hence, no emission inventory can be compiled. Many of these sources may contribute significant amounts of PAHs and related material in localized situations.

It must be kept in mind that most of the above emission estimates are highly speculative, although the orders of magnitude of the emissions may indicate an approximation of the significance of individual sources. The relative importance of various sources of PAH emissions has been altered in the last several years and will probably be refined as new, more reliable information becomes available.

Table 3-2. Estimated benzo[a]pyrene emissions to the atmosphere (after USNAS 1972 and Suess 1976).

Source type	Benzo[a]pyrene emissions ($t.a^{-1}$) United States	% of total	Worldwide	% of total
INDUSTRIAL PROCESSES				
Coke production	192	15	1033	20
	6	<1	12	<1
FUEL COMBUSTION (STATIONARY SOURCES)				
Utilities and industrial				
- coal	431	34	2376	47
- oil	2	<1	5	<1
- gas	2	<1	3	<1
Residential				
- fuelwood	40	3	220	4
TRANSPORTATION				
Gasoline-powered cars	10	<1	16	<1
Gasoline-powered trucks	12	<1	29	<1
Diesel-powered trucks and buses	≈0.4	<1	?	
SOLID WASTE INCINERATION				
Enclosed incineration				
- commercial and industrial	23	2	69	1
- municipal, apartment, etc.	11	1	33	4
MISCELLANEOUS				
Forest fires and agricultural burning	140	11	420	8
Coal refuse fires	340	26.5	680	13
Municipal, domestic and industrial open fires	74	6	148	3
TOTAL	1283		5044	

Table 3-3. Estimated annual emission of total PAHs from sources emitting more than 1 tonne per annum in the United States (from Ramdahl 1981).

Source type	Estimated emission ($t.a^{-1}$)	Percent of PAH total emissions
INDUSTRIAL PROCESSES		
Coke production	630	7
Aluminum smelting	2100	25
Carbon black production	3	<0.1
Asphalt roofing	15	0.2
Asphalt paving - hot mix	4	<0.1
FUEL COMBUSTION (STATIONARY SOURCES)		
Utilities		
- dry bottom boilers (lignite coal)	14	0.1
(bituminous coal)	7	0.1
- wet bottom boilers (lignite coal)	4	<0.1
- oil-fired intermediate boilers	380	4
Industrial		
- dry bottom boilers (bituminous coal)	41	0.5
- stoker-fired boilers (bituminous coal)	7	0.1
Residential		
- fuelwood	3800	45
- bituminous coal	100	1
- gas	6	0.1
- distillate oil	5	0.1
TRANSPORTATION		
Mobile sources (unspecified)	250	3
MISCELLANEOUS		
Forest fires	1000	12
UNSPECIFIED SOURCES		
Other stokers and boilers firing coal	10	0.1
Other combustion of gas	3	<0.1
TOTAL	8379	

Table 3-4. Escimated annual PAH emissions in the United States by source type (from Peters et al. 1981).

Source type	Estimate emissions ($t.a^{-1}$)	Percent of PAH total emissions	Reference
INDUSTRIAL PROCESSES			
Coke production	632	5.7	Eimutis et al. (1978) Siebert et al. (1978)
Carbon black production	3.1	<0.1	Serth and Hughes (1977)
Charcoal manufacturing			
- uncontrolled batch kilns	0.8	<0.1	Moscowitz (1978)
- continuous furnace production	0.7	<0.1	Moscowitz (1978)
Asphalt production			
- saturators	0.2	<0.1	Siebert et al. (1978)
- air blowing	0.2	<0.1	Siebert et al. (1978)
- hot road mix	3.9	<0.1	Khan and Hughes (1977)
Barium chemicals			
- black ash rotary kiln	0.3	<0.1	Reznik and Toy (1978)
FUEL COMBUSTION SOURCES (STATIONARY SOURCES)			
Utilities			
- coal	12.9	0.1	DeAngelis et al. (1979)
- oil	0.3	<0.1	Supernant et al. (1976)
- gas	0.3	<0.1	Supernant et al. (1976)
Industrial			
- coal	69.0	0.6	DeAngelis et al. (1979)
- oil	1.3	<0.1	Supernant et al. (1976)
- gas	2.1	<0.1	Supernant et al. (1976)
- wood/bark	1.2	<0.1	Peters and Thalman (1980)
- bagasse	0.3	<0.1	Supernant et al. (1976)
Residential			
- fuelwood		34.8	DeAngelis et al. (1979)
- primary heating	1383		
- auxiliary heating	2376		
- fireplaces	78		
- coal-fired	102	0.9	DeAngelis and Reznick (1979)
- oil-fired	7.4	<0.1	Siebert et al. (1978)
- gas-fired	9.8	<0.1	Siebert et al. (1978)
TRANSPORTATION			
Gasoline-powered cars	2160.8	19.6	Siebert et al. (1978)
Diesel-powered cars	1.2	<0.1	Siebert et al. (1978)
Diesel-powered trucks	103.5	0.9	Siebert et al. (1978)
SOLID WASTE INCINERATORS			
Municipal	0.3	<0.1	Hangebrauck et al. (1967); Siebert et al. (1978)
Industrial	55.8	0.5	Hangebrauck et al. (1967); Siebert et al. (1978)
MISCELLANEOUS			
Agricultural open burning	1190	10.8	Hangebrauck et al. (1967); Chi and Zanders (1977)
Prescribed burning	1071	9.7	Chi et al. (1979) Yamate (1974)
Forest wildfires	1478	13.4	Chi et al. (1979) DeAngelis et al. (1979)
Coal refuse piles	28.5	0.3	Chalekode and Blackwood (1978)
Land clearing waste burning	171	1.6	Clark (1974)
Structural fires	86		Clark (1974) DeAngelis et al. (1979)
TOTAL	11 031		

Table 3-5. Estimated Canadian annual benzo[a]pyrene emissions to the atmosphere[α] (from Lao 1982).

Source type	Estimated emission ($kg.a^{-1}$)	Reference
INDUSTRIAL PROCESSES		
Coke production	12 000	D
Aluminum reduction	4000-6000	E
Petroleum catalytic cracking	500-1000	B
Asphalt and carbon electrode manufacture	1	B
FUEL COMBUSTION (STATIONARY SOURCES)		
Utilities		
- coal	≈40	F
Industrial		
- coal	≈0.2	F
- oil	≈20	B
- oil (commercial/industrial)	≈150	B
- gas	≈4	A
- gas (commercial/industrial)	≈120	A
Residential		
- coal	≈1	A
- oil	≈30	B
- gas	≈25	A
TRANSPORTATION		
Gasoline-powered cars	400	G
Diesel-powered trucks and buses	20	G
Motorcycles	400-600	G
Tire wear	1100	G
MISCELLANEOUS		
Tobacco smoke	2	C
TOTAL	≈19 000-22 000	

[α] Emissions from forest fires and other uncontrolled burning have not been included. In 1976, B[a]P-emissions from this source approximated 7500-100,000 kg in Ontario (Reference I).

A - Statistics Canada Report - Cat. No. 57-207, Aug. 1978.
B - Statistics Canada Report - Cat. No. 45-208, May 1978.
C - Statistics Canada Report - Cat. No. 32-022, Dec. 1977.
D - Statistics Canada Report - Cat. No. 45-002, June 1978.
E - Environment Canada Report, EPS 3-AP-77, 1977.
F - Statistics Canada Report - Cat. No. 26-206, July 1978.
G - Statistics Canada Report - Cat. No. 57-218, June 1978.
H - Falk et al. (1960) and Gold (1975).
I - Ontario Ministry of Natural Resources Annual Report, 1977.

3.2.2 WATERBORNE SOURCES

3.2.2.1 Municipal Effluents

"Municipal effluent" is a rather broad term which generally refers to wastewaters or other liquids, partially or completely treated or in their natural state, which are discharged from sanitary sewers, storm drainage systems, sewage treatment plants and/or combinations thereof. These wastewaters may often receive effluents from industries that discharge various wastes directly into the sewer. Industrial wastes and surface runoff may contribute substantially to the PAH loading of municipal effluents. According to Borneff and Kunte (1965) concentrations of PAHs in municipal effluents usually parallel the relative amount of effluent contributed by industry and are dependent upon the specific industrial source.

It is estimated that municipal waste contributes 0.3 million $t.a^{-1}$ of hydrocarbons to the world's oceans, approximately 5% of the total hydrocarbons entering the oceans (McAuliffe 1976). Domestic effluents have been found to contain from 22 to 2416 $\mu g.L^{-1}$ of various PAHs (Table 3-6, 3-7). The large range in PAH content measured most probably reflects variation in source strength, type of sampling, duration and time of sampling as well as season. The amount of rainfall, and hence the amount of surface runoff, significantly influence the PAH content of wastewater with levels of individual PAHs increasing by several orders of magnitude during episodes of heavy rain. However, other factors such as land usage, drainage characteristics and the elapsed time between storm events may influence the characteristics of PAHs in stormwater runoff.

The oxidative action of biological treatment processes is not sufficient to remove PAHs completely, although some will be adsorbed onto particulate matter and will be removed in the sludge (Andelman and Suess 1970; Andelman and Snodgrass 1974). Sludge from wastewater treatment plants has been found to contain high levels of PAHs (Borneff and Kunte 1965; McIntyre et al. 1981). In their study of wastewater sludge collected from twelve wastewater treatment facilities in the United Kingdom, McIntyre et al. (1981) found elevated concentrations of the six PAHs examined (Table 3-8). Although exhibiting a considerable degree of variation, the results implied that relatively high concentrations of PAHs tend to occur in sludges of predominantly domestic origin. However, the highest concentrations were found in sludges from treatment works receiving industrial effluents.

Polycyclic aromatic hydrocarbons of relatively high molecular weight appear to be extensively adsorbed to particulate matter, whereas smaller PAH molecules, being more soluble in water, are less extensively adsorbed to particulates and hence are only slightly reduced in the treated effluent (Wedgewood and Cooper 1956). When treatment facilities do not function properly, hydrocarbon levels in both sludge and final effluents may increase (Wedgewood and Cooper 1954).

Table 3-6. Polycyclic aromatic hydrocarbons in municipal effluents[a] (after Borneff and Kunte 1965).

	PAH Content $\mu g.L^{-1}$			
Compound	Domestic effluents	Sewage Dry weather	Heavy rain	Sewage (high percentage industry)
Fluoranthene	273-2416	352	16 350	2660-3420
Pyrene	1763	254	16 050	2560-3120
Benz[a]anthracene	167-319	25	10 360	343-1360
Benzo[b]fluoranthene	114-202	39	9 910	525-870
Benzo[j]flouranthene	37-205	57	10 790	1100-1740
Benzo[k]flouranthene	31-193	22	4 180	336-460
Benzo[a]pyrene	38-74	1	1 840	100-368
Benzo[ghi]perylene	40-219	4	3 840	120-480
Indeno[1,2,3-cd]pyrene	22-238	17	4 980	476-930

[a] Terms such as domestic effluents, sewage etc. were not defined in the original reference. It is assumed that "domestic effluents" comprise all solid and liquid organic wastes produced by residents and delivered to a treatment facility and that "sewage" designates a combination of domestic effluent and collected surface runoff.

Table 3-7. PAH content of sewage[α] (from Grzybowski et al. 1983).

Compound[β]	Concentration Range[γ] $\mu g.L^{-1}$
Fluorene	0.5-2.0
Phenanthrene	0.5-10.0
Anthracene	0.1-1.0
Fluoranthene	0.5-5.0
Pyrene	11.0-27.0
Chrysene/Benz[a]anthracene	0.1-24.0
Benzo[j]fluoranthene	14.0-52.0
Benzo[e]pyrene	1.0-5.5
Benzo[b]fluoranthene/Perylene	0.7-2.0
Benzo[b]fluoranthene	1.0-5.5
Benzo[a]pyrene	0.6-6.5
Dibenz[a,c]anthracene	0.8-4.5
Dibenz[a,h]anthracene	0.0-6.6
Benzo[ghi]perylene	0.0-10

[α] The term sewage was not defined. No information on source of material was available.

[β] Compounds identified and quantitated by high pressure liquid chromatography.

[γ] Range of concentration in 15 sewage samples.

3.2.2.2 Industrial Effluents

Some industrial processes result in the production of high levels of PAHs that enter the environment not only through emissions to the atmosphere (see Section 3.2.1), but often through inclusion in effluents that may be discharged directly to the aquatic environment or into wastewater systems. Industrial operations involving the combustion of fossil fuels can generate significant levels of PAHs (Andelman and Snodgrass 1974). The normal use of material produced by pyrolysis (coal tar, creosote, anthracene oil, coal tar pitch, and carbon black) and/or the burning and disposal of these materials, may also release PAHs to the environment.

Table 3-9 illustrates the levels of B[a]P found in the effluents from some industries. According to Andelman and Suess (1970), the industries producing high levels of B[a]P are coke production (up to 1000 $\mu g.L^{-1}$), shale oil processing (up to 320 $\mu g.L^{-1}$), and acetylene production (up to 100 $\mu g.L^{-1}$). Other industries that may produce significant levels of PAHs in effluents include petroleum refineries, aluminum smelters, plastics and dyestuff industries, high temperature furnaces or incinerators, the lime industry, gas works, and coal liquefaction facilities.

With respect to PAH-containing effluents from aluminum smelters, Cretney et al. (1982) identified several PAHs in surface sediments and age-dated cores from Kitimat Arm in northern British Columbia. Elevated levels of PAHs in dated cores corresponded in time to the construction and early production years of the Alcan aluminium smelter. In addition, the distribution of PAHs in surface sediments of northern Kitimat Arm was consistent with the smelter being the source.

3.2.2.2.1 Energy-related industries

Coal

Coal is generally considered to have a low PAH content compared with its burned or pyrolyzed products (Radding et al. 1976). Approximately 40-75% of the carbon in subbituminous and bituminous coals is aromatic, the aromaticity increasing with coal rank (Gavalas 1982). Lignites and subbituminous coals contain nuclei with one to three condensed rings, while bituminous coals contain mostly 2 to 4 condensed rings. Woo et al. (1978) identified several PAHs in Iowa and Illinois coal, including phenanthrene, benz[a]anthracene, benzo[e]pyrene, dibenzo[b,def]chrysene, perylene and benzo[ghi]perylene.

Analysis of sediment and particulate matter in a stream in the Rhondda Fawr Valley of South Wales, U.K., where extensensive coal mining was carried out in the 19th Century, revealed elevated levels of several PAHs (anthracene 0.6-17.6, fluoranthene 0.6-13.8, pyrene 0.7-21.3,

Table 3-8. Concentrations of PAHs in sewage sludge samples from two different sewage treatment plants (from McIntyre et al. 1981).

Source	Sample No.	PAH Concentration $\mu g.L^{-1}$ wet weight ($\mu g.g^{-1}$ dry weight)						
		Fluoranthene	Benzo[a]pyrene	Benzo[a]fluoranthene	Benzo[k]fluoranthene	Benzo[g,h,i]perylene	Indeno[1,2,3-cd]pyrene	Total
A	1	20-30 (0.47-0.71)	16-20 (0.38-0.48)	16-20 (0.38-0.48)	8-12 (0.19-0.29)	12-16 (0.29-0.38)	12-16 (0.29-0.38)	84-114 (0.20-2.71)
	2	20-30 (0.61-0.91)	20-30 (0.61-0.91)	16-20 (0.48-0.61)	16-20 (0.48-0.61)	12-16 (0.36-0.48)	12-16 (0.36-0.48)	96-132 (2.92-4.00)
	3	20-30 (0.34-0.51)	16-20 (0.28-0.34)	12-16 (0.20-0.27)	16-20 (0.27-0.34)	8-12 (0.14-0.20)	8-12 (0.14-0.20)	80-110 (1.35-1.86)
	4	16-20 (0.35-0.44)	8-12 (0.28-0.27)	12-16 (0.27-0.35)	4-8 (0.08-0.18)	8-12 (0.18-0.27)	12-16 (0.27-0.35)	60-84 (1.33-1.87)
	5	20-30 (1.76-2.35)	16-20 (0.59-1.18)	8-12 (1.18-1.76)	12-16 (0.29-0.59)	8-12 (0.23-0.34)	8-12 (0.59-1.18)	72-102 (2.06-2.91)
B	1	60-80 (1.76-2.35)	20-40 (0.59-1.18)	40-60 (1.18-1.76)	10-20 (0.29-0.59)	20-40 (0.59-1.18)	20-40 (0.59-1.18)	170-280 (5.00-8.24)
	2	320-400 (9.14-11.43)	240-320 (6.86-9.14)	140-320 (6.86-9.14)	80-160 (2.29-4.57)	240-320 (6.86-9.14)	160-240 (4.57-6.86)	1280-1760 (36.6-50.3)
	3	80-100 (3.33-4.16)	40-60 (1.67-2.50)	40-60 (1.67-2.50)	20-40 (0.83-1.67)	40-60 (1.67-2.50)	20-40 (0.830-1.67)	240-360 (10.0-15.0)
	4	60-80 (0.74-0.99)	10-20 (0.12-0.24)	5-10 (0.06-0.12)	5-10 (0.06-0.12)	5-10 (0.06-0.12)	5-10 (0.06-0.12)	90-140 (1.00-1.73)
	5	100-150 (3.13-4.69)	40-60 (1.25-1.88)	60-80 (1.88-2.50)	20-40 (0.63-1.35)	40-60 (1.25-1.88)	60-80 (1.88-2.50)	320-470 (10.0-14.7)
	6	160-240 (4.44-6.66)	80-160 (2.22-4.44)	80-160 (2.22-4.44)	40-80 (1.11-2.22)	40-80 (1.11-2.22)	40-80 (1.11-2.22)	440-800 (12.2-22.2)
	7	100-150 (2.81-4.21)	80-100 (2.24-2.81)	60-80 (1.69-2.24)	20-40 (0.56-1.12)	80-100 (2.24-2.81)	40-60 (1.12-1.69)	380-530 (10.66-14.88)

A - Sewage treatment works that receive predominantly domestic sewage and a low proportion of industrial effluents.

B - Sewage treatment works that receive a relatively higher proportion of industrial effluents.

Table 3-9. Benzo[a]pyrene content of some industrial effluents (after Andelman and Suess 1970).

Industry	Source of Waste Water	B[a]P concentration $\mu g.L^{-1}$
Shale oil	after treatment for dephenolization	2-320
Coke by-products	after oil separation	6.5-290
	after biochemical treatment	12-16
Coke or oil gas works	before discharge to sewer	340-1000
Oil-gas works	after oil separation	3-30
Oil refinery	after oil separation	-
Acetylene production	not indicated	0.015-0.10
Ammonium sulfate	after cooling and settling	≈10

benzo[c]fluorene 0.2-7.1, chrysene 1.1-56.8, B[a]P 2.7-29.3, dibenz[a,c]anthracene 0-7.3, benzo[ghi]perylene 0-6.0 $\mu g.g^{-1}$ dry sediment) (John and Nickless 1977). These high levels were attributed to contamination of the stream bed with coal from coal washing carried out in the area (John et al. 1979).

Coal conversion encompasses more than one hundred specific processes designed to produce liquid, gaseous and refined solid products as energy sources or as chemical feedstocks (Howard-Smith and Werner 1975; Cochran 1976). These processes typically result in the production of significant quantities of PAHs (Dailey 1977; Huffstetler and Rickert 1977).

The distribution of compound types present in the distillates from two coal liquefaction processes is summarized in Table 3-10. The polyaromatic content of these distillates ranges from approximately 5 to 40% of the crude oil weight, depending on process type, coal feed and distillate boiling range. A significant proportion (4-22%) of the product consists of HACs. Numerous amino-substituted PAHs and C_1-C_5 alkylated amino-PAHs were identified in heavy distillate material from coal liquefaction (Later et al. 1981). Total concentrations ranged from approximately 200 $\mu g.L^{-1}$ for aminonaphthalenes to approximately 20 $\mu g.L^{-1}$ for aminochrysenes and aminobenzanthracenes. Various amino PAHs were also identified in coal gasifier tars (collected from a low Btu-coal gasifier) and coal oil (a Comparative Research material used for biological assays and analytical methods), particularly 2-aminonaphthalene, at the $\mu g.g^{-1}$ level (Tomkins and Ho 1981). Tars from condensates produced by the gasification of an Illinois No. 6 coal in a Synthane gasifier contain significant quantities of sulfur-containing heterocyclic compounds, predominantly thiophene-based aromatic compounds (Lee et al. 1979c).

Phenolic compounds are considered to be the major organic constituents of by-product and process waters from coal conversion (Ho et al. 1976); however, numerous PAHs have been identified (Table 3-11). Wastewater concentrations of PAHs are usually in the sub-$mg.L^{-1}$ range. Wastewaters generated during the scrubbing of gasifiers from the gasification of coal at temperatures lower than 1000-1200°C contain significant quantities of heavy organic oils and tars (Patelunas et al. 1979). Included among these oils are several PAHs. Aqueous effluents were found to contain 4- or 5-ring PAHs at the saturation level and PAHs with 3 or fewer rings at the 1-10% saturation level (Herbes et al. 1976). Effluent concentrations of 1-10 $mg.L^{-1}$ total PAHs were reduced 30-80% by wastewater treatment.

Underground coal gasification produces naphthalene- and thiophene-type aromatic compounds which, under the appropriate conditions, may be transported to ground water (Campbell et al. 1979; Stuermer et al. 1982). Humenick and Mattox (1978), examining groundwater before and after underground coal gasification, found that total organic carbon levels in groundwater increased 10-fold from

Table 3-10. Distribution of organic constituents in synthetic crude oil distillates (from Woodward et al. 1976).

	Percent Weight of Distillate Constituents					
Process Coal Distillate	Synthoil[α] W. Virginia 207°-363°C	COED[α] W. Kentucky 205°-380°C	COED Utah 204°-381°C	Synthoil W. Virginia 363°-531°C	COED W. Kentucky >380°C	COED Utah >381°C
Saturate	16	25	27.8	9.7	23.8	25.8
Monoaromatic	27.3	42	25.1	4.7	25.1	14.4
Diaromatic	21.6	13	17.5	22.6	24.3	18.4
Polyaromatic	7.9	5.4	7.1	41.1	20	25.1
Heteroaromatic	22.2	4.4	15.2	15.6	4.5	7.4
Distillate % of crude	42.6	54.2	45.4	27.3	24.2	40.3

[α] For a description of the processes used in coal conversion the reader is referred to Guerin (1978).

Table 3-11. Polycyclic aromatic hydrocarbons in coal and shale conversion[α] waters (after Guerin et al. 1976 and Fruchter et al. 1977).

Compound	Concentration ($mg.L^{-1}$)		
	Synthane gasification condensate	Solvent-refined coal raw process water	Simulated in situ shale report by-product water
Naphthalene	0.2	5	0.1
2-Methylnaphthalene	1.3	2	0.3
1-Methylnaphthalene	<0.1	NR	0.1
2,6-Dimethylnaphthalene	<0.1	NR	<0.1
1,3+1,6-Dimethylnaphthalene	0.1	NR	0.2
1,5+2,3-Dimethylnapthalene	<0.1	NR	0.1
1,2-Dimethylnaphthalene	<0.1	NR	<0.1
Dimethylnaphthalenes	NR[β]	2.3	NR
2-Isopropylnaphthalene	NR	0.7	NR
1-Isopropylnaphthalene	NR	2	NR
Acenaphthalene	NR	<0.1	NR
Acenapthene	IR[γ]	NR	<0.1
Dimethylbiphenyls	NR	0.7	NR
Fluorene	<0.1	0.3	0.2
9,10-Dihydroanthracene	<0.1	NR	<0.1
9-Methylfluorene	NR	0.3	NR
1-Methylfluorene	ND[δ]	0.2	0.2
Anthracene/phenanthrene	ND	1.1	0.3
2-Methylanthracene	ND	NR	0.2
1-Methylphenanthrene	ND	0.2	0.1
9-Methylanthracene	ND	NR	0.4
Methylphenanthrene	NR	0.3	NR
Fluoranthene	ND	0.4	<0.1
Dihydropyrene	NR	<0.1	NR
Pyrene	ND	0.6	0.1
Benzo[a]fluorene	ND	NR	<0.1
Benzo[b]fluorene	ND	NR	<0.1
1-Methylpyrene	ND	NR	0.1
Benz[a]anthracene	ND	NR	<0.1
Chrysene/triphenylene	ND	NR	<0.1

[α] For a description of the processes used in coal conversion the reader is referred to Guerin (1978).

[β] NR - not reported.

[γ] IR - incomplete resolution.

[δ] ND - not detected.

approximately 20 to 200 $mg.L^{-1}$. In a later study, Mattox and Humenick (1980) found approximately 140 $\mu g.L^{-1}$ total PAHs in groundwaters in the vicinity of underground coal gasification operations. The total concentrations in groundwater for the various PAHs were as follows: 105 $\mu g.L^{-1}$ for 2-ring compounds, 22 $\mu g.L^{-1}$ for 3-ring PAHs, 7 $\mu g.L^{-1}$ for 4-ring PAHs, and 3 $\mu g.L^{-1}$ for 5-ring PAHs. The extent of groundwater contamination was found to be directly related to the water solubility of the PAHs.

As discussed previously, a significant industrial point source of atmospheric PAHs is the emissions arising from the production of coke and coal tar (see Section 3.2.1.1). Depending upon the technology used, significant quantities of PAHs may also be released to the aquatic environment. Harbor sediments receiving aqueous and solid effluents from a gas works and iron works in Japan were examined by Kawakami and Nishimura (1976). Coke ovens were in operation at both these locations and B[a]P levels as high as 89 $\mu g.g^{-1}$ were found in sediments close to the plants. Large volumes of quenching water used to cool the coke after the removal from the ovens became contaminated with PAHs and were often discharged to the aquatic environment without adequate treatment. Effluent and surrounding sediment at a coking plant in the United States were found to contain more than 170 different identifiable PAHs (Griest and Herbes 1978). Sediment levels were found to be 10^3-10^4 times greater than levels in adjacent waters and were slightly different in distribution, suggesting a differential adsorption and/or persistence. In their investigation of PAH contamination of Sydney Harbour, Nova Scotia, EPS (1982) found very high levels of PAHs (12 measured) in sediments near the outfall from a steel industry/coke oven complex. Levels were recorded as high as 2829 $\mu g.g^{-1}$ (dry weight). Eight km away the levels were still high at 40-50 $\mu g.g^{-1}$; even at the mouth of the harbor, a distance of 16 km from the source, levels exceeded 7 $\mu g.g^{-1}$. Concentrations of B[a]P ranged from 108.5 $\mu g.g^{-1}$ near the outfall to 0.37 $\mu g.g^{-1}$ in a separate area of the harbor and dropped to 0.026 $\mu g.g^{-1}$ approximately 16 km from the source.

Creosote, a distillate fraction of coal tar, is used extensively in the treatment of wood to prevent rot and attack by wood-boring organisms. Approximately 300 compounds have been identified in coal tar, including numerous PAHs and HACs, and it is suspected that as many as 10 000 compounds may be present (Gibb 1978). Although PAH content varies with the source of material (Table 3-12), concentrations are relatively higher in creosote than in coal tar (the feedstock) or wood preservative sludge (the waste product).

A number of studies examine the release to water of creosote from treated wood (Hochman 1967; Webb 1975; Miller 1977). A study carried out in Atlantic Canada (Eaton and Zitko 1978) examined the influence of treated wharves and bridges on adjacent sediments and shellfish. Substantial amounts of "creosote-like" hydrocarbons were identified by fluorimetry in surrounding sediments and shellfish, and

Table 3-12. PAH content of creosote, creosote sludge and coal tar (from Uthe 1979).

Compound	PAH content ($g.kg^{-1}$)												
	Lijinsky et al. 1957	Lijinsky et al. 1963	Tarrer et al. 1977	Guin et al. 1977	Prather et al. 1977	Colley 1974 A[β]	Colley 1974 B[β]	Colley 1974 C[β]	Eaton and Zitko 1978	Nestler 1974	Lorenz and Gjovik 1972	Lao et al. 1975 Coal tar	Lao et al. 1975 Wood preservative sludge
Anthracene	6.2	12.1	43	43	18	-	-	-	-	20	15	-	-
Benz[a]anthracene	2.8	2.8	-	-	-	-	-	-	31	-	-	43[δ]	5
Benzo[b]chrysene	-	0.5	-	-	-	-	-	-	-	-	-	23[ζ]	5
Benzo[j]fluoranthene	-	0.29	-	-	-	-	-	-	-	-	-	1	0.3
Benzo[k]fluoranthene	-	0.20	-	-	-	-	-	-	-	-	-	33	7
Benzo[g,h,i]perylene	-	-	-	-	-	-	-	-	-	-	-	18[η]	-
Benzo[a]pyrene	0.12	0.18	-	-	-	-	-	-	-	-	-	33	3.6
Benzo[e]pyrene	-	0.17	-	-	13	18	38	-	-	-	-	-	2.5
Chrysene	1.3	1.14	-	-	-	-	-	-	-	30	-	-	5[ε]
Fluoranthene	7.8	23.5	9.6	5.5	-	39	70	111	70	100	34	54	26
Perylene	0.04	0.04	-	-	-	-	-	-	-	-	-	3	-
Phenanthrene	47.9	36.6	186	186	125[α]	83[γ]	155[γ]	200[γ]	193	210	107	81[γ]	15[γ]
Pyrene	4.2	8.4	2.6	2.6	-	31	53	81	64	85	22	47	24
Naphthalene	-	-	151	51	93	128	42	28	-	30	158	-	-
2-Methylnaphthalene	-	-	1.3	1.3	87	53	40	6	-	12	30	-	-
1-Methylnaphthalene	-	-	3.8	3.8	39	33	31	12	-	9	-	-	-
1,6-Dimethylnaphthalene	-	-	3.9	3.9	-	15	14	4	-	20	-	-	-
2,3-Dimethylnaphthalene	-	-	1.9	1.9	-	-	-	-	-	-	-	-	-
Acenaphthene	-	-	60	60	70	53	83	75	67	90	31	-	-
Dibenzofuran	-	-	67	67	-	40	62	51	-	50	11	-	-
Fluorene	-	-	103	103	53	34	59	56	48	100	31	27	6
9,10-Dihydroanthracene	-	-	24	24	-	-	-	-	-	-	-	2	1
3-Methylphenanthrene	-	-	9.8	9.8	-	7	13	18	-	30	-	-	8
4,5-Methylenephenanthrene	-	-	25	25	-	-	-	-	-	-	-	3[θ]	-
2-Methylanthracene	-	-	2.4	2.4	-	16	32	39	-	40[θ]	-	-	8
9-Methylanthracene	-	-	1.2	1.2	-	-	-	-	-	-	-	-	-
2,3-Benzofluorene	-	-	-	-	-	13	13	31	-	20[ι]	-	20[ι]	-

[α] Single analysis.

[β] Marine creosotes - Specific gravities A-1.070, B-1.092, C-1.108.

[γ] Phenanthrene and anthracene.

[δ] Contains chrysene, triphenylene and all benzanthracenes.

[ε] Contains chrysene and triphenylene.

[ζ] Contains benzo[a]chrysene and phenylenepyrene.

[η] Contains benzo[g,h,i]perylene and anthanthrene.

[θ] Contains methyl anthracenes and methylphenanthrenes.

[ι] All benzofluorenes.

significant levels of particular PAHs have been identified by GC/MS. For example, in sediment close to a creosoted wharf, levels as high as 25.7 $\mu g.g^{-1}$ fluoranthene, 35 $\mu g.g^{-1}$ pyrene, and 48 $\mu g.g^{-1}$ benz[a]-anthracene (wet weight) were reported. Samples remote from creosoted timbers had levels of PAHs several orders of magnitude lower. In an examination of black, oily leachate that was seeping into a spring-fed river, Black et al. (1980) determined that the source of contamination was an abandoned wood preservation facility. Several spills of creosote were recorded during the operation of the facility between 1902 and 1949. Sediment samples were collected above (control site) and below (up to 45 km) the source, and concentrations of several PAHs were determined (concentrations of pyrene, B[a]A and B[a]P appear in Table 3-13). In general, the concentration of individual PAH compounds declined rapidly below the source but they did not reach background levels. The decline in concentrations tended to be asymptotic, with the result that the river sediments contained levels above the background over a considerable distance. Some studies have shown that the concentrations of individual and total PAHs in creosote from creosote-treated wood aged for several years, were comparable to those of the original creosote (Stasse 1967; Colley 1974). The sediments surrounding piers that had been treated with coal tar contained elevated levels of PAHs compared with the background levels (Lake et al. 1979).

Petroleum

Crude petroleum and many petroleum products contain an extremely complex mixture of several thousand organic compounds, including many PAHs and HACs. Hydrocarbons account for approximately 75% of the weight of crude oil, with the remainder being composed of oxygen-, nitrogen- and sulfur-containing organic compounds (Speers and Whitehead 1969). This chemical complexity has frequently hampered the identification and quantification of individual PAHs and HACs in petroleum and petroleum products; some general trends in hydrocarbon composition have, however, been identified.

The four American Petroleum Institute (API) reference oils (two crude and two distillate fuel oils) that have been designated for biological studies have been extensively analyzed for their chemical composition. The weight distribution of aromatic compounds in these oils is presented in Table 3-14. As the molecular weight of the aromatic fraction increases, the percentage by weight decreases. There is also a significant contribution from sulfur-containing aromatic compounds to the crude oils. The PAH content of the four reference oils is presented in Table 3-15. The concentrations of individual PAHs differed significantly among the oils tested. In general, lower-molecular-weight compounds, such as naphthalene, were present in higher concentrations than higher-molecular-weight compounds. Processing significantly increases the relative proportions of many of the PAHs. Consistent with the theories of PAH formation (see Section 3.1),

Table 3-13. Distribution of 3 PAH compounds identified in sediment samples collected downstream from an abandoned wood preservation facility (after Black et al. 1980).

Sample Site	PAH content ($\mu g.g^{-1}$ wet weight) P	B[a]A	B[a]P	PAH content ($\mu g.g^{-1}$ organic content) P	B[a]A	B[a]P
1 (Control)	.016	.00	.00	ND	ND	ND
2	231.00	61.67	15.82	5.26	1.35	0.35
3	ND	14.58	7.41	ND	0.50	0.25
4	15.26	4.19	1.16	1.53	0.42	0.11
5	ND	8.57	4.50	ND	0.28	0.15
6	8.51	4.48	1.35	0.39	0.20	0.061
7	4.00	3.71	1.20	0.12	0.11	0.036
8	0.38	0.72	0.29	0.014	0.027	0.011
9	0.35	1.02	0.40	0.011	0.031	0.012

ND - not determined.

Table 3-14. Aromatic compound distribution in API reference oils (from Pancirov 1974).

Compound classification	No. of aromatic rings	Percent Weight of Constituents[a] South Louisiana crude	Kuwait crude	No. 2 fuel oil	Bunker C oil
Benzenes	1	3.9	4.8	10.3	1.9
Indans-Tetralins	1	2.4	2.2	7.3	2.1
Dinaphthalene-benzenes	1	2.9	2.0	4.6	2.0
Naphthalenes	2	1.3	0.7	5.9	2.6
Acenaphthenes	2	1.4	0.9	3.8	3.1
Acenaphthalenes	2	2.8	1.5	5.4	7.0
Phenanthrenes	3	0.9	0.3	-	11.6
Pyrenes	4	-	-	-	1.7
Chrysenes	4	-	0.2	-	-
Benzothiophenes	2	0.5	5.4	0.9	1.5
Dibenzothiophenes	3	0.4	3.3	-	0.7
Indenothiophenes	3	-	0.6	-	-
Total aromatics		16.5	21.9	38.2	34.2

[a] Estimated by mass-spectrographic analysis.

Table 3-15. PAH content of API reference oils (from Pancirov and Brown 1975).

Compound	PAH Content ($mg.L^{-1}$)			
	South Louisiana crude	Kuwait crude	No. 2 fuel oil	Bunker C oil
Naphthalene	400	400	4 000	1 000
1-Methylnaphthalene	800	500	8 200	2 800
2-Methylnaphthalene	900	700	18 900	4 700
Dimethylnaphthalenes[a]	3600	2000	31 100	12 300
Trimethylnaphthalenes[a]	2400	1900	14 400	8 800
Fluorenes	200	100	3 600	2 400
Phenanthrene	70	26	429	482
1-Methylphenanthrene	111	-	173	43
2-Methylphenanthrene	144	89	1 677	823
Fluoranthene	5.0	2.9	37	240
Pyrene	3.5	4.5	41	23
Benz[a]anthracene	1.7	2.3	1.2	90
Chrysene	17.56	6.9	2.2	196
Triphenylene	10	2.3	1.4	31
Benzo[ghi]fluoranthene	1	<1	-	-
Benzo[b]fluoranthene	<0.5	<1	-	-
Benzo[j]fluoranthene	<0.9	<1	-	-
Benzo[k]fluoranthene	<1.3	<1	-	-
Benzo[a]pyrene	0.75	2.8	0.6	44
Benzo[e]pyrene	2.5	0.5	0.1	10
Perylene	34.8	<0.1	-	22
Benzo[ghi]perylene	1.6	<1	-	-
Approximate total	8700	5740	92 560	34 010

[a] Isomers not specified.

alkylated PAHs are present in higher concentrations than unalkylated PAHs (Blumer and Youngblood 1975; Pancirov and Brown 1975). Two crude oils (heavy Lloydminster and light Medicine River oils from the Alberta Basin, Canada) were analyzed for PAH content (Table 3-16) (Chmielowiec et al. 1980). Concentrations were highest for 3- and 4-ring structures in the aromatic concentrates of both oils.

The catalytic cracking of crude oils to produce hydrocarbon fuels and other refined petroleum products results in the production of PAHs. These PAHs may be either contained in the resulting products (Table 3-15) or released to the environment via atmospheric emissions and waterborne effluents. Much of the PAHs produced during catalytic refining becomes concentrated in the high-boiling residual oils (Bunker C or No. 6 fuel oil) and asphalts. Release of PAHs to the atmosphere in catalyst-regeneration flue gas has been examined by Sawicki et al. (1965). Scrubbing of this flue gas may also result in PAH release via waterborne effluents. In general, the PAH content of treated refinery effluents appears to be relatively low (Andelman and Snodgrass 1974; Kawakami and Nishimura 1976; Searl et al. 1979). An efficiently operating activated sludge unit appears to reduce the PAH content of refinery effluent by approximately two orders of magnitude (Table 3-17) (Searl et al. 1979).

Cutting oils (e.g. anthracene oil) and other lubricants prepared improperly from coal or petroleum wastes may contain high levels of PAHs (Uthe 1979). For example, Thony et al. (1976) found B[a]P in concentrations as high as 10 $\mu g.g^{-1}$ in anthracene oil.

It has been estimated that 85% of the PAHs produced by a gasoline engine is retained in the crankcase oil (USNAS 1972). In their examination of used crankcase oil, Peake and Parker (1979) identified approximately 90 PAHs and 20 sulfur-containing heterocyclic aromatic compounds. The concentration of B[a]P, chrysene, benzo[c]phenanthrene, benz[a]anthracene, cyclopenta[c,d]pyrene and benzo[ghi]perylene totalled approximately 10 $\mu g.mL^{-1}$ oil. A large fraction of the PAHs identified were alkylated. Concentrations of sulfur-containing compounds totalled approximately 10 $\mu g.mL^{-1}$ oil.

Shale Oil

The production of shale oil[a] involves the use of large quantities of both shale and water with the resultant release of substantial amounts of spent shale and process water. For example, a shale oil facility producing one million barrels of oil per day would

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[a] Shale oil is defined as the organic mixture of substances that is created by the retorting process (Futrell 1980).

Table 3-16. Distribution of PAH ring classes in Lloydminster and Medicine River crude oils[α] (from Chmielowiec et al. 1980).

Number of rings[β]	Percent Weight	
	Lloydminster	Medicine River
3	48	49
4	23	25
>4	19	15
retained on column[γ]	10	11

[α] deasphaltened distillation residues boiling above 35°C.

[β] model compounds used for calibration purposes 3-ring-phenanthrene, anthracene
4-ring-pyrene, chrysene
5-ring-dibenzo[a,c] pyrene

[γ] high pressure liquid chromatography, silica-R(NH)s column eluted with hexane.

Table 3-17. PAH content of petroleum refinery effluents (after Searl et al. 1979).

Compound	Concentration ($\mu g.L^{-1}$) DMF Effluent[α]	ASU Effluent[β]
Fluoranthene	17	ND (0.2)
Pyrene	106	0.07
Benz[a]anthracene	31	ND (0.03)
Chrysene	16	ND (0.03)
Triphenylene	11	ND (0.03)
Methylbenz[a]anthracene[γ]	20	0.10
Dimethyl/ethylbenz[a]anthracene[γ]	7	0.07
Benzo[ghi]fluoranthene	6	ND (0.4)
Benzo[b]fluoranthene	ND (3)[δ]	ND (0.1)
Benzo[j]fluoranthene	ND (6)	ND (0.2)
Benzo[k]fluoranthene	ND (5)	ND (0.2)
Perylene	2.6	0.14
Benzo[a]pyrene	20	0.57
Benzo[e]pyrene	11	0.65
Methylbenzo[a]pyrene[γ]	11	0.27
Methylbenzo[e]pyrene[γ]	7	0.38
Benzo[ghi]perylene	6	0.36
Coronene	ND (0.1)	ND (0.01)
Indenopyrene[γ]		ND (0.02)

α DMF effluent - dual media filter (after the American Petroleum Institute separator).

β ASU effluent - activated sludge unit effluent.

γ Isomers not specified.

δ ND () - not detected (detection limit using gas chromatography - ultraviolet spectroscopy).

have to dispose of approximately 600 million tonnes of spent shale (Kuhn 1974). Shale oil is known to contain numerous PAHs and HACs; however, the content varies depending upon location (Futrell 1980). Although the B[a]P content of crude shale oil is approximately 3 $\mu g.g^{-1}$, the content in spent shale has been found to be no greater than 40 $\mu g.kg^{-1}$ (Coomes 1976). Weathered spent shale contains approximately 15-115 $\mu g.kg^{-1}$ B[a]P (Bonomo 1974). Little information is available on the PAH content of shale-oil-plant wastewaters. In a simulated study (Fruchter et al. 1977), water recovered from a shale retort contained a PAH fraction composed of essentially the same general molecular-weight distribution as wastewaters from coal gasification and solvent-refined wastewaters (Table 3-11). Concentrations of PAHs identified were in the sub-$mg.L^{-1}$ range.

Concentrations of B[a]P were determined in the wastewaters of a shale-oil processing plant in Estonia, U.S.S.R. (Veldre et al. 1979). The extraction of phenols with butyl acetate was found to be the most efficient process of wastewater treatment with respect to B[a]P; although recorded levels of B[a]P in various wastewaters were low (Table 3-18), no data were given on the quantity of wastewater discharged and hence, no estimation of PAH emission rate can be made.

In summary, it appears that from the limited data available, the PAH content of various fossil fuels and refined products varies dramatically (Table 3-19). Crude petroleum contains approximately 1 $mg.L^{-1}$ B[a]P, while shale- and coal-derived crude oil contains approximately three times as much as crude petroleum. The B[a]P content of petroleum products ranges from 0.4 $mg.L^{-1}$ for gasoline to 2000 $mg.L^{-1}$ for catalytically produced petroleum pitch. Other refined coal-based products, such as creosote and coal-tar pitch, may also contain substantial quantities of B[a]P as well as other PAHs and HACs.

3.3 ENTRY INTO THE AQUATIC ENVIRONMENT

3.3.1 ATMOSPHERIC DEPOSITION

3.3.1.1 Transport and Stability in the Atmosphere

The majority of high-molecular-weight PAHs (> 3 or 4 rings) released to the atmosphere from combustion and pyrolytic sources are associated with airborne particles. At elevated temperatures significant quantities of PAHs may exist in the vapor phase (cf. Pupp et al. 1974). However, once removed from the high-temperature source, PAHs will be rapidly and quantitatively adsorbed to soot and other particulate matter (Thomas et al. 1968; Natusch and Tomkins 1978). Adsorption appears to occur through hydrogen bonding to oxygen functional groups situated on the surface of the particles (Thomas et al. 1968). Using theoretical models, Natusch and Tomkins (1978) predicted that PAHs would be preferentially adsorbed to the surface of

Table 3-18. Benzo[a]pyrene content of treated effluents from a shale-oil facility (after Veldre *et al.* 1979).

Source	Benzo[a]pyrene content ($\mu g.L^{-1}$) Kohtla-Järve Plant, Estonia
Water before dephenolization	20-68
Water after dephenolization	1.6-2
Extraction with butylacetate	0
Extract of crude phenols	11 880-13 500
Water before trickling filters	0.16
Water after trickling filters	0.12

Table 3-19. Benzo[a]pyrene content of energy-related materials (after Guerin 1978).

Material	Approximate B[a]P content ($mg.L^{-1}$)
1. Crude oils	
petroleum	1
shale-derived	3
coal-derived	3
2. Petroleum products	
gasoline	0.4
motor oil (new)	0.03
motor oil (used)	4
diesel fuel	0.05
No. 2 heating oil	0.03
asphalt	2
petroleum pitch (catalytic)	2 000
3. Miscellaneous	
creosote	200
coal tar	3 000
coal tar pitch	10 000
raw shale	0.015
processed shale	0.03
bituminous coal	<0.001

fine particles. In the context of this document, fine particles are defined as those particles having an aerodynamic diameter less than 2 μm (NRCC 1982). Adsorption to co-entrained particulate matter during or following emission from a source is the primary gas-to-particle conversion process for PAHs (Cabaniss and Linton 1981; Schure and Natusch 1982). Eiceman and Vandiver (1983) found that PAHs adsorbed rapidly to fly ash collected from a municipal incinerator and a coal-fired power plant. Irreversible adsorption occurred at concentrations below 30 $\mu g.g^{-1}$ PAH g^{-1} fly ash. At concentrations above 30 $\mu g.g^{-1}$ adsorption was governed by vapor pressure.

Experimental and field evidence suggests that a large fraction of PAHs emitted from various sources to the atmosphere is associated with fine particles. For example, Broddin et al. (1977) found that approximately 94% of the PAHs present in coke-oven emissions were associated with particles <3 μm. In their study of a steel-mill coke-oven emissions, Miguel and Rubenick (1979) found that over 60% of B[a]P and benzo[ghi]perylene was found in particles <0.7 μm. Approximately 50% of the B[a]P in fly ash emitted from a coal-fired power plant was found in particles <0.1 μm (Stahley, as quoted by Natusch 1978). Although a significant fraction of low-molecular-weight PAHs can be found in the vapor phase in the exhaust from gasoline-powered automobiles, the majority of higher-molecular-weight compounds are associated with small particles. For example, 95% of the B[a]P and benzo[ghi]perylene and 90% of several other PAHs were found in particles <1.0 μm (Pederson et al. 1980). Several PAHs measured in the air of a traffic tunnel with heavy vehicular traffic were found predominantly in particles <0.1 μm (Miguel and Rubenick 1979; Handa et al. 1980); this led the authors to speculate that the PAHs measured were associated with vehicle exhaust and not with dust entrainment.

Once a PAH-containing aerosol is released to the atmosphere, its size distribution will continually change depending upon the contributions of airborne particles from different sources, atmospheric turbulence and other meteorological conditions, as well as the chemical stability of the adsorbed PAHs. In general, the PAHs found in ambient environments are also associated primarily with fine particles; although in some cases PAHs, especially those of low molecular weight, can be found in the vapor phase (cf. DeMaio and Corn 1966; Kertesz-Saringer et al. 1971; Albagli et al. 1974; Pierce and Katz 1975; Cautreels and Van Cauwenberghe 1978; Miguel and Friedlander 1978; Van Vaeck and Van Cauwenberghe 1978; Handa et al. 1980; Mainwaring and Stirling 1981). Depending upon the type and strength of a particular source, significant quantities of PAHs may also be found in airborne particles larger than 3-5 μm (Katz and Pierce 1976).

Particle size has a significant influence upon the residence time of atmospheric aerosols (NRCC 1982). In the absence of precipitation, the residence time of airborne particles is 4-40 days for particles <1 μm, and 0.4-4 days for particles 1-10 μm (Esmen and Corn

1971). Slinn (1978) calculated that the average residence time of 0.1 to 1.0 μm particles in the troposphere was approximately 1 week in winter and 2 weeks in summer; that is, residence time is approximately equal to the wet-deposition removal time. Thus, disregarding chemical degradation, PAHs associated with fine particles may have significant residence times in the atmosphere and may be transported over relatively long distances. This phenomenon has been demonstrated by a number of authors (cf. Lunde and Bjorseth 1977; Daisey et al. 1981; Gschwend and Hites 1981; Tan and Heit 1981). Concentrations of PAHs in aerosols originating from continental western Europe and the United Kingdom were 26 to 29% higher than those in aerosols originating from northern Norway or found in stationary air masses in southern Norway (Bjorseth et al. 1979). Daisey et al. (1981) found average concentrations of POM and PAHs in arctic aerosols to be similar to those reported for other remote sites in the northern hemisphere but concentrations during the spring sampling period were much higher than during the summer sampling period. The presence of fly ash in the collected samples, as well as seasonal differences in the concentrations of organic material and ^{210}Pb, and in meteorology, indicated to the authors that the principal source of POM and PAHs was fossil fuel combustion in the mid-latitudes during the spring sampling period. Shaw et al. (1979), in their survey of arene and alkane hydrocarbons in nearshore Beaufort Sea sediments, postulated that long-range transport from anthropogenic sources was the major source of PAHs in the sediments. Other sources, such as offshore and onshore oil seeps and coal outcrops probably contributed to PAH sediment loading in specific locales.

It is generally accepted that PAHs in the atmosphere can be degraded. Borneff and Knerr (1959) estimated that the reduction in B[a]P in air amounted to 20-50% per day. During the last 10 years attention has focused on the determination of the rates and extent of degradation, along with the environmental and health significance of the ultimate products of such reactions.

The two principal oxidizing species in ambient air are believed to be the HO radical, formed by the photolysis of NO_2, H_2O, CO and simple organic compounds, and ozone, formed by the photolytic combination of molecular and atomic oxygen (Radding et al. 1976). The major influence of PAH structure on photolytic reactivity is an increased reactivity of alkyl-substituted PAHs towards electrophilic reactions with oxidants. The reaction of PAHs with singlet molecular oxygen appears to be less important because of the relatively low concentration and rapid quenching mechanisms for singlet oxygen in air; however, McCoy and Rosenkranz (1980) have reported that singlet oxygen can react with PAHs to form mutagenic products. The authors reasoned that levels of singlet oxygen will increase in polluted air in response to increased levels of oxides of nitrogen released from various sources.

Numerous laboratory studies have attempted to examine the stability of PAHs under simulated conditions. Most early investigators

studied the photolysis of PAHs in non-aqueous solutions. The relevance of nonaqueous solution photochemistry to photolysis of PAHs adsorbed to particulate matter is probably remote. Early gas-solid photooxidation experiments used PAHs as solids adsorbed to various substrates but most of these studies used light sources that did not adequately simulate sunlight and used oxidant concentrations far in excess of those found in the ambient environment.

In recent years, several experiments have been performed in which PAHs, in pure solid form or deposited on various solid substrates or particles, have been exposed to light, oxygen, ozone, nitrogen oxides and sulfur oxides. For example, Lane and Katz (1977) and Katz et al. (1979), using artificial light simulating sunlight and low levels of ozone (0.4 $mg.m^{-3}$), studied the photomodification of several PAHs spread on a thin film on glass or adsorbed on cellulose. The extent of degradation varied with the compound examined. For example, in the presence of ozone in the dark, anthracene, benz[a]anthracene, dibenz[a,h]anthracene and B[a]P were readily degraded. Benzo[a]pyrene (half-life ≈ 0.6 h) was the most rapidly degraded, while pyrene (≈ 16 h), benzo[b]fluoranthene (≈ 53 h) and benzo[k]fluoranthene (≈ 35 h) were less reactive. Isomeric differences in stability were also found (e.g. B[a]P was more rapidly degraded than B[e]P (≈ 8 h); dibenz[a,h]anthracene (≈ 3 h) was more readily degraded than dibenz[a,c]anthracene (≈ 4 h). For several PAHs studied, the presence of light increased the rate of degradation. However, there did not appear to be a significant difference in half-lives of B[a]P exposed to ozone in the dark (≈ 0.62 h) or exposed to light and ozone (≈ 0.58 h). In general, the rate of decomposition was found to decrease with exposure time, suggesting that the surface-adsorbed layer reacted quickly but hindered the decomposition of subsurface layers. The reaction of B[a]P deposited on glass fiber filters with ozone in the dark was studied by Pitts et al. (1980). At 0.1 ppm ozone, a 47% conversion was recorded after one hour (Van Cauwenberghe et al. 1980) with a maximum attainable conversion of 57%. Identifiable reaction products included ring-cleavage compounds (e.g. dialdehydes, dicarboxylic acids) and disubstituted benzo[a]pyrenes (e.g. dihydroxy compounds and quinones). Small amounts of benzo[a]pyrene-4,5-epoxide were also found (Pitts et al. 1980).

Falk et al. (1956) speculated that adsorption to soot had a stabilizing effect on the degradation of B[a]P. Recently, Korfmacher et al. (1979, 1980a, 1980b) found that some PAHs (e.g. B[a]P, pyrene, anthracene), when adsorbed in the vapor phase onto fly ash particles, were highly resistant to photodegradation. In general, conversion rates were less than 20% for the PAHs studied. This led the authors to conclude that the chemical transformation of adsorbed PAHs in the atmosphere may be determined largely by the rate of thermal reactions (e.g. interaction with atmospheric gases), with photochemistry playing a relatively minor role. Hughes et al. (1979) found that pyrene and B[a]P adsorbed on alumina, coal fly ash and silica gel were not photodegraded

in the presence of air. Using a fluidized bed photoreactor, Daisey et al. (1982) reported that pyrene, adsorbed to coal fly ash (concentration ≈ 0.6 $mg.g^{-1}$ substrate; surface concentration ≈ 0.1 $mg.m^{-2}$) and exposed to air, had a half-life of approximately 20 h in the absence of light and at approximately 7 h in the presence of light. However, studies with pyrene adsorbed to Carbosieve S, a pure carbon substance with a large surface area (860 $m^2.g^{-1}$), found a half-life for pyrene (concentration ≈ 70 $mg.g^{-1}$; surface concentration ≈ 0.08 $mg.m^{-2}$) of approximately 23 h in either the presence or absence of light. Since the substrate used was a high porosity and light-absorptive material with a large surface area, it was speculated that the light could not penetrate into the interior of the particle where much of the pyrene was adsorbed.

The degradation of PAHs in the presence of atmospheric gases other than ozone has been recently examined. Pitts et al. (1978) and Pitts (1979) examined the reactivity of B[a]P, perylene and pyrene adsorbed on glass fiber filters in the presence of 2 $mg.m^{-3}$ NO_2 in air in the dark. In the presence of a small amount of nitric acid, considerable yields of nitro-PAHs were found (approximately 60% for an 8-h exposure). The rates of reaction for PAHs adsorbed to various substances decreased in order of silica gel, fly ash, alumina and carbon, irrespective of the adsorbed PAH (Jaeger and Hanus 1980). Brorström et al. (1983) exposed PAH-containing suspended particulate matter to NO_2 during actual high-volume sampling of ambient air. Comparison of control and NO_2-exposed samples indicated that B[a]P and B[a]A were degraded by 19 and 12%, respectively, upon exposure to 0.1 $mg.m^{-3}$ NO_2 during high-volume sampling for 24 hours at -5 to 0°C. Hughes et al. (1979) detected the presence of mono- and dinitro- B[a]P and pyrene in the presence of 200 $mg.m^{-3}$ NO_2. Several sulfonated and oxygenated products were found when the PAHs were exposed to 330 $mg.m^{-3}$ SO_3. No significant reactions were observed with similar concentrations of NO or SO_2. In addition, none of the reactions were affected by visible light. Butler and Crossley (1981) exposed PAHs adsorbed to particulate matter (soot generated from combustion under laboratory conditions) to 20 $mg.m^{-3}$ NO_x and found some degradation. Individual PAHs exhibited different reactivities with half-lives ranging from approximately 4 days (dibenzo[def,mno]chrysene) to approximately one month (phenanthrene, dibenzo[ghi,pqr]perylene, coronene). Benzo[a]pyrene and benzo[e]pyrene had half-lives of 7 and 24 days, respectively. Numerous nitro-PAHs were detected, including 6-nitrobenzo[a]pyrene, 7-nitrobenz[a]anthracene and nitrochrysene derivatives. Exposure to 13 $mg.m^{-3}$ SO_2 did not result in any significant modification of the PAH studied.

Hence, superimposing the different susceptibilities to degradation during transport through the atmosphere onto an already complex assemblage of PAHs and HACs emitted from one or more sources, leads to an exceedingly complex spectrum of compounds undergoing continual change in composition as a function of input, transport,

reactivity and removal. The experimental results on degradation of PAHs in the presence of atmospheric oxidants suggest that serious miscalculations of atmospheric loading may occur if one relies solely on the measurements of a single compound. In addition, there has been recent concern regarding the loss of some PAHs caused by volatilization (cf. Lao and Thomas 1979; Peters and Seifert 1980; Yamasaki et al. 1982) and chemical degradation in the presence of co-existing gaseous pollutants (cf. British Carbonization Research Association 1979; Lee et al. 1979a; Van Cauwenberghe et al. 1980; Brorström et al. 1983) during the long-term atmospheric sampling of particulate matter.

3.3.1.2 Deposition Processes

The identification of PAHs and HACs in marine and freshwater sediments and some biota (cf. Youngblood and Blumer 1975; Hites et al. 1980; Stich and Dunn 1980; Wakeham and Farrington, 1980; Wakeham et al. 1980b; Clarke and Law 1981; Heit et al. 1981; Hites 1981; Tan and Heit 1981; Venkatesan and Kaplan 1982) has led many authors to speculate that the atmospheric deposition of PAH-containing particles to surface waters and adjacent watersheds is a significant route of entry for these compounds into the aquatic environment and may be responsible for much of the background concentration in the absence of other identifiable sources.

There are presently few quantitative data on the entry of PAHs and HACs into the aquatic environment from the atmosphere. In their study of dated sediment cores, Gschwend and Hites (1981) and Hites and Gscwend (1982) reported that PAHs are delivered uniformly to sites distant from identifiable sources of the northeastern United States at a flux of 0.8 to 3 $ng.cm^{-2}.a^{-1}$ (Table 3-20). Sites closer to urban areas had a much higher flux (average of 35 $ng.cm^{-2}.a^{-1}$), probably because of the combined input from atmospheric deposition and surface runoff of PAH-containing material. The authors' data indicate that PAH fluxes are 5-10 times greater than those of 80 years ago, but that these inputs have diminished by a factor of 2 during the last two decades. Eisenreich et al. (1981) estimated the total input of total PAHs to the Great Lakes at approximately 484 $t.a^{-1}$ (Table 3-21). Benzo[a]pyrene input was estimated at approximately 24 $t.a^{-1}$.

The mean B[a]P content of particulate matter in nonurban and urban continental aerosols is approximately 8 and 38 $ng.g^{-1}$ (annual averages), respectively (USNAS 1972). Maritime aerosols have a B[a]P content of approximately 17 $ng.g^{-1}$ (annual average). Benzo[a]pyrene may, however, represent only 1-20% of the total PAHs present in airborne particles (USNAS 1972). For example, Lunde and Bjorseth (1977) found that B[a]P contributed only 3-7% to the total PAH content of aerosols collected in Norway. It has been reported (Strand and Andren 1979; Andren and Strand 1981) that B[a]P content of aerosols sampled over Lake Michigan, USA, represented approximately 10% of the total PAHs measured.

Table 3-20. PAH fluxes to sediments from 5 remote sites in the northeastern United States and 3 urban sites (from Gschwend and Hites 1981; Hites and Gschwend 1982).

Site	Time interval	PAH flux ($ng.cm^{-2}.a^{-1}$)								
		Phenanthrene	Anthracene	C_1-phenanthrene	Fluoranthene	Pyrene	Benz[a]-anthracene	Chrysene/ Triphenylene	B[e]P[β]	B[a]P[γ]
REMOTE SITES										
Lake Superior	1955-present	0.3	0.03	0.3	1	0.6	0.3	1	0.9	0.4
	1930-1955	0.2	0.02	0.2	0.9	0.5	0.3	1	0.9	0.3
	1870-1920	0.06	0.004	0.08	0.3	0.1	0.7	0.3	0.2	0.07
Isle Royale, Lake Superior	1974-present	0.4	0.01	0.5	0.4	0.3	0.2	0.8	0.8	0.2
	1951-1955	1	0.05	2.5	1	0.7	0.2	0.7	0.9	0.2
Sommes Sound, Mount Desert Island, Maine	1960-present	2	0.2	1	5	4	2	2	2	2
	1940-1960	4	0.4	4	8	5	3	4	2	2
	1880-1940	0.4	<0.02	<0.2	0.4	0.4	<0.05	<0.2	0.2	0.2
Hadlock Lower Pond, Mount Desert Island, Maine	1950-present	2	0.1	2	4	3	0.6	1	0.8	0.6
	1920-1950	0.3	0.04	-	0.3	0.2	0.04	0.1	0.1	0.06
Coburn Mountain Pond, Maine	1975-present	2	0.2	4	4	3	0.7	2	2	0.7
	1943-1947	8	0.5	12	11	8	3	6	7	4
	1898-1901	0.8	0.07	1	0.5	0.3	0.2	0.9	0.4	0.1
Averages	Preser	1	0.1	1.5	3	2	0.8	1.5	1.5	0.8
	≈1950	3	0.2	4.5	4	3	1.5	2.5	3	1.5
	≈1900	0.4	0.03	0.4	0.4	0.3	0.1	0.2	0.5	0.1
URBAN SITES										
Boston Outer Harbor	1900-present	24	5.6	17	37	39	19	23	14	17
Buzzards Bay, Mass.	1940-present	18	2	-	53	48	37	37	-	140
Pettaquamscutt River, Mass.	1940-present	46	5	36	93	93	42	42	-	130
Averages		30	4	25	55	55	30	35	≈25	≈30

[α] Includes all $C_{20}H_{12}$ isomers except perylene.

[β] B[e]P = Benzo[e]pyrene.

[γ] B[a]P = Benzo[a]pyrene.

Table 3-21. Total deposition of PAHs to the Great Lakes (from Eisenreich et al. 1981).[a]

Compound	Lake ($t.a^{-1}$)					Total
	Superior	Michigan	Huron	Erie	Ontario	
Total PAH	163	114	118	51	38	484
Anthracene	4.8	3.4	3.5	1.5	1.1	14.3
Phenanthrene	4.8	3.4	3.5	1.5	1.1	14.3
Pyrene	8.3	5.9	6.1	2.6	1.9	24.8
Benz[a]anthracene	4.1	2.9	3.0	1.5	1.1	12.6
Perylene	4.8	3.3	3.4	1.5	1.1	14.1
Benzo[a]pyrene	7.9	5.6	5.8	2.5	1.8	23.6

[a] Deposition based on concentration of PAHs in air as reported in the literature (those references consulted may be found in Eisenreich et al. 1980).

Using a B[a]P content of 17 $ng.g^{-1}$ particulate matter and a PAH content of 340 $ng.g^{-1}$ particulate matter (Pierce and Katz 1975) (i.e. assuming B[a]P accounts for 5% of total PAH content), a rough estimate of the magnitude of entry of B[a]P and PAH entry into the world's oceans from the atmosphere may be made. The input of nonsilicate anthropogenic particles from the atmosphere to the oceans has been estimated at 10^8 $t.a^{-1}$ (Robinson 1976). Hence, the input of B[a]P and PAHs would be 1700 $t.a^{-1}$ and 34 000 $t.a^{-1}$, respectively.

3.3.2 WATER-BASED DISCHARGES

Materials containing PAHs and HACs may directly enter the aquatic environment via several water-based discharges such as 1) the release of crude oil and/or petroleum products during exploration, production, transport and natural seepage, and 2) the release of PAHs and associated compounds from materials used in water (e.g. creosoted pilings, piers, containment facilities).

World-wide oil production in 1971 was estimated to be 2.5×10^9 t. Assuming a B[a]P content in crude oil of 1 $mg.L^{-1}$ (Guerin 1978), approximately 2.5×10^3 t of B[a]P may be potentially released to the total environment. Pancirov (1974) estimated the total PAH content (including naphthalenes) of two API reference crude oils to be 3 to 6%, by weight, indicating a total potential PAH release of 75×10^6 to 150×10^6 t, based on 1971 estimates. It is interesting to note that the PAH content of No. 2 fuel oil and Bunker C oil are 15 and 20%, respectively, by weight (Pancirov 1974).

Estimates of the quantity of petroleum hydrocarbons entering the world's oceans from water-based discharges range from 1×10^6 $t.a^{-1}$ to 5×10^6 $t.a^{-1}$ (Table 3-22). Assuming the above estimated B[a]P and PAH contents for crude oil, the amount of B[a]P entering the oceans would be 1-5 $t.a^{-1}$, while the amount of PAHs would be 30×10^3 to 300×10^3 $t.a^{-1}$.

According to Grossling (1976), world oil production in 1972 was 2.8×10^9 t. Approximately 3.6×10^6 t of crude oil and some of its liquid products entered the world's oceans through man-made activities. Based on 1972 production estimates, the amount of oil discharged to the oceans as a result of oil industry accidents and tanker cleaning operations approximates 0.9×10^6 t and 0.4×10^6 t, respectively. The amount of offshore and onshore natural seepage was estimated at (0.2-6.0) $\times 10^6$ t and (0.8-24) $\times 10^6$ t, respectively. Natural offshore seepage of crude oil was estimated at 0.5×10^6 t, based on 1980 projected production figures (USNAS 1975).

Creosote and coal tar, used in the treatment of wharves, bridges, pilings, containment areas, etc., contain high levels of PAHs. Elevated levels of several compounds have been found in sediments and

Table 3-22. Estimates of the quantities of petroleum hydrocarbons entering the world's oceans (from Connell and Miller 1980).

Source	Estimates for year indicated ($t \times 10^6\ a^{-1}$)				
Water-based discharges					
Tankers (LOT)[a]	3.0	0.31	1.63	0.1	0.2
Tankers (non-LOT)	1.5	0.77		0.6	0.3
Dry docking	-	0.25		-	0.15
Bilge discharge	0.5	0.50		0.05	-
Accidents	-	0.30		0.2	0.15
Offshore production	-	0.08		0.15	0.20
Natural oil seeps	-	0.60		-	0.60
Land-based discharges					
Refineries	2.0	0.2	-	0.3	0.02
Precipitation runoff	-	2.50	0.45	0.5	2.40
Waste oils	-				
Sewage	-				
Atmospheric deposition	-	0.60	9.0	-	0.60
Total	7.0	6.11	11.08	1.90	4.62
Reference	McIntyre and Whittle (1977)	USNAS (1975)	GESAMP (1977)	Wardley-Smith (1973)	USNAS (1975)

[a] LOT - load on top.

biota in the vicinity of such structures (Zitko 1975; Dunn and Stich 1976; Dunn and Fee 1979).

3.3.3 LAND-BASED DISCHARGES

Estimating the quantity of PAHs released from sources such as municipal and industrial operations and surface runoff is extremely difficult because of the lack of reliable data on the actual concentration of compounds in effluents, and a general lack of information on the total volume of material discharged. In addition, non-point as well as point sources must be considered in computing total input.

Assuming a global wastewater discharge (domestic wastewater and liquid industrial effluent) of 24 x 10^{13} $L.a^{-1}$ (Neff 1979) and a B[a]P and PAH content of 0.07 and 6 $\mu g.L^{-1}$, respectively (Borneff and Kunte 1965), yields a loading to the aquatic environment of approximately 17 $t.a^{-1}$ B[a]P and 1.4 x 10^{3} $t.a^{-1}$ total PAHs.

Although surface runoff can contain significant quantities of PAHs (cf. Herrmann 1981), reliable information on the quantities of PAHs entering the aquatic environment from such sources is limited. The concentrations of B[a]P and total PAHs in surface waters are in the range of 0.0006-0.35 $\mu g.L^{-1}$ (mean 0.08) and 0.24-2.5 $\mu g.L^{-1}$ (mean 0.9), respectively (USEPA 1980). The total runoff from the North American continent is estimated at 3 x 10^{15} $L.a^{-1}$, which includes some domestic and industrial liquid effluents (Neff 1979). Using a ratio of 1:3 to convert from North American to worldwide values (Neff 1979), B[a]P and total PAH loading to the aquatic environment would be 960 $t.a^{-1}$ and 10 800 $t.a^{-1}$, respectively.

The concentration of PAHs in groundwaters is normally very low, ranging from non-detectable to 0.04 $\mu g.L^{-1}$ (USEPA 1980), although levels may be elevated in particular cases because of contamination from landfills, waste disposal sites, underground coal gasification, etc. It is not expected that groundwater discharge would contribute significantly to the PAH total loading of the aquatic environment; it may, however, be of importance on a localized scale.

The land-disposal of certain materials containing PAHs and associated compounds may increase aquatic loading in special cases. For example, Grossling (1976) estimated that approximately 2.3 x 10^{6} $t.a^{-1}$ of petroleum hydrocarbons are added to the world's oceans as a result of the disposal of spent lubricants. The total concentration of all identifiable PAHs in used crankcase oil was reported to be approximately 83 $mg.L^{-1}$ (Peake and Parker 1979) while the B[a]P content was 0.4 $mg.L^{-1}$. Assuming the above PAH contents are representative of spent lubricants, approximately 0.9 $t.a^{-1}$ B[a]P and 190 $t.a^{-1}$ total PAHs may reach the world's oceans.

3.3.4 BIOSYNTHESIS

Evidence for the complete biosynthesis of PAHs by microorganisms, algae, fungi and higher plants is still ambiguous (see Section 3.1.3). However, assuming that some limited biosynthesis does occur, one may estimate the quantity of PAHs that could be released to the aquatic environment. Borneff et al. (1968) reported a biosynthetic rate by the alga Chlorella of 0.6 $\mu g.kg^{-1}$ dry algal biomass and 67 $\mu g.kg^{-1}$ dry algal biomass for B[a]P and total PAHs, respectively. The annual production of organic carbon in the world's oceans is estimated at 4×10^{10} $t.a^{-1}$ (Koons and Monaghan 1976). Hence, rough estimates of B[a]P and total PAH production due to biosynthesis would be 24 and 2680 $t.a^{-1}$, respectively.

3.3.5 ESTIMATES OF TOTAL INPUT

It is estimated that the total amount of B[a]P and total PAHs entering the aquatic environment from all sources considered approximates 2700 $t.a^{-1}$ and 80 000-200 000 $t.a^{-1}$, respectively (Table 3-23). Atmospheric deposition appears to contribute the largest overall input of B[a]P to the aquatic environment. Water-based discharges (i.e. petroleum tankers, accidents, offshore production and natural seeps) appear to be the largest source of total PAHs; however, a large fraction of petroleum and associated products are composed of PAHs other than 4-, 5- and 6-ring polycyclic compounds. The B[a]P content of such material is expected to be much lower than the total PAH content. It must be emphasized that the above estimates are based on meagre and often imprecise data and hence, numerous assumptions and extrapolations had to be made. As discussed previously, B[a]P may not be a representative PAH because of its chemical reactivity. The different physical and chemical properties of individual PAHs in environmental media will alter the composition and quantity of the PAHs as a group. Numerous sources, although not considered to be significant on a worldwide basis, may be very important in localized areas.

3.4 FATE IN THE AQUATIC ENVIRONMENT

3.4.1 ABIOTIC CYCLING

3.4.1.1 Solubility, solubilization and sorption

The solubilities of most PAHs and HACs in pure water are low (see Section 2.2); hence, it has been implicitly assumed that these hydrophobic compounds exist solely in the particulate phase in fresh or salt waters. However, in natural waters, a concentration-dependent exchange equilibrium exists between adsorbed and soluble states; while this equilibrium favors the particulate phase in most cases, a soluble fraction of certain PAHs and HACs can exist in dilute solutions.

Table 3-25. Estimated inputs of benzo[a]pyrene and total PAHs to the aquatic environment from various sources.

Source	Estimated input ($t.a^{-1}$)	
	Benzo[a]pyrene	Total PAHs
Atmospheric deposition	1 700	34 000
Water-based discharges	1-2	30 000-150 000
Land-based discharges		
Domestic and industrial effluents	17	1 400
Surface runoff	900	10 500
Spent lubricant disposal	1	190
Biosynthesis	24	2 000
Approximate total	2 700	80 000-230 000

In natural waters and wastewaters, numerous compounds have been found that may solubilize PAHs and HACs. Dissolved and colloidal compounds have been shown to solubilize PAHs by incorporating them into micelles. However, a critical micellar concentration for such a compound must be reached before the solubility of PAHs is affected. Such critical concentrations are, in general, several times those generally found in the aquatic environment (Il'nitsky and Ershova 1970; Il'nitsky et al. 1971; Il'nitsky et al. 1976b).

A wide variety of organic compounds have been found to increase the solubility of PAHs in water. They include purines (Weil-Malherbe 1946), butyric and lactic acids (Ekwall and Sjoblom 1952), nitrogen-containing organic compounds (Eisenbrand 1971), acetone, ethanol and dioxane (Suess 1972). Boehm and Quinn (1973) examined the solubilization of some petroleum hydrocarbons in seawater by humic-like organic matter and found no effect on the solubilities of anthracene and phenanthrene. However, the increased solubility of B[a]P in humic acid-rich water has been demonstrated by Gjessing and Berglind (1981). Recently, Carlberg and Martinsen (1982) demonstrated that phenanthrene and fluoranthene were quantitatively complexed by humic material in water; equilibria were rapidly established. In addition, the authors found that 90% of the humic material, along with the complexed PAHs, passed through a resin adsorption column, implying low recoveries of PAHs if resins are used to concentrate materials from humic-rich waters.

Numerous authors have noted the ability of B[a]P and other PAHs to concentrate by sorption onto activated carbon, calcareous material, silica, glasses and plastics (cf. Andelman and Suess 1970). Meyers and Quinn (1973) studied the nature of the sorptive process using aromatic hydrocarbons with bentonite clay in saline solution and found that sorption could be described as a physical adsorption of the van der Waals type. Indigenous humic substances previously adsorbed to clay particles interfered with the uptake of hydrocarbons by masking the binding sites or reducing available surface area. Since the association forces binding PAHs and other hydrocarbons to inorganic particles are weak, biological activity and dissolution - even from particles incorporated into sediment - could release these compounds and make them more available for uptake by aquatic organisms. This process could be accelerated by the disruption of sediment layers by natural and anthropogenic activities.

Of greater importance than their adsorption to inorganic particles appears to be the sorption of PAHs onto suspended organic matter. Herbes (1977) studied the sorptive properties of autoclaved yeast cells and found that a significant fraction of anthracene would be associated with detrital and living organic matter in natural waters containing a moderate amount of suspended organic solids. Whereas a powdered calcite concentration of 500 $mg.l^{-1}$ resulted in a 30% adsorption of B[a]P (Suess 1968), only 25 $mg.l^{-1}$ of yeast cells were

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Source	Estimated input ($t.a^{-1}$)	
	Benzo[a]pyrene	Total PAHs
Atmospheric deposition	1700	34 000
Water-based discharges	1-5	30 000-150 000
Land-based discharges		
Domestic and industrial effluents	17	1 400
Surface runoff	960	10 800
Spent lubricant disposal	1	190
Biosynthesis	24	2 680
Approximate total	2700	80 000-200 000

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required to adsorb anthracene to a similar extent (Herbes 1977). Montmorillonite clay, in concentrations representative of natural waters, adsorbed only 1-5% anthracene, whereas yeast cells, at equivalent concentrations, sorbed 15-65% anthracene (Herbes 1977).

Smith et al. (1977, 1978), Karickhoff et al. (1979), Southworth (1979a), Means et al. (1980, 1982) and Banwart et al. (1982) have demonstrated a high correlation between the sorption of PAHs and HACs onto suspended particles and bottom sediments, and organic carbon content (Tables 3-24, 3-25 and 3-26). In general, sorption increases as organic carbon content increases. The organic sorption partition coefficient (ratio of sorption partition coefficient and fraction mass of organic carbon in the particle) increased linearly with organic carbon content (Karickhoff et al. 1979; Means et al. 1982). There was also a high correlation between the organic sorption partition coefficient and the octanol-water partition coefficient. Octanol-water partitioning provided a much better estimate of particulate-water partitioning than did water solubility for the PAHs tested. In addition, sorption showed only a slight dependence upon ionic strength.

In their studies of the fate of PAHs in enclosed marine ecosystems, Hinga et al. (1980) and Lee et al. (1982) found that the predominant process for removal of compounds such as B[a]P and B[a]A was either direct adsorption to bottom sediments after turbulent mixing, or adsorption onto suspended particles and subsequent sedimentation. For those compounds studied, photochemical oxidation, volatilization and microbial degradation were of little significance. An exception was 7,12-dimethylbenz[a]anthracene, which underwent photolytic oxidation before it could sediment out of the water column. Microbial degradation was the significant removal process for photolytic products.

From their survey of PAHs in the Tamar Estuary, U.K., Readman et al. (1982) were able to categorize those PAHs identified with respect to their physical-chemical behavior. One group was composed of low-molecular-weight compounds (naphthalene, phenanthrene, anthracene) while the second group was made up of higher-molecular-weight compounds (fluoranthene, pyrene, chrysene, B[a]A, B[k]F, B[b]F, B[a]P). For the first group, a complex distribution throughout the estuary with no significant correlation with salinity or suspended particles was observed. The authors proposed that volatilization was the major loss mechanism from the water column. Concentrations of the higher-molecular-weight compounds exhibited significant correlations with suspended particles, with highest concentrations at maximum turbidity.

Volatilization appears to play an important role in the short-term removal of petroleum hydrocarbons (including PAHs) from estuaries (Knap and Williams 1982); however, the most important process affecting the long-term removal from estuaries is adsorption to estuarine sediments.

Table 3-24. Sorption of some PAHs and HACs on clays and natural sediments (after Smith et al. 1977, 1978).

Compound	Sediment[α]	Total organic carbon %	Sorption[β] partition coefficient K_p
Benz[a]anthracene	Coyote Creek	1.4	26 200
	Des Moines River	0.6	8 300
	Searsville Pond	3.8	20 700
Benzo[a]pyrene	Ca-montmorillonite clay	0.06	17 000
	Coyote Creek	1.4	76 000
	Des Moines River	0.6	42 000
	Searsville Pond	3.8	165 000
Quinoline	Ca-montmorillonite clay	0.06	8
	Coyote Creek	1.4	11
Benzo[f]quinoline	Coyote Creek	1.4	1 300
Carbazole	Ca-montmorillonite clay	0.06	3
	Coyote Creek	1.4	175
7H-dibenzo[c,g]carbazole	Coyote Creek	1.4	20 500
Benzo[b]thiophene	Ca-montmorillonite clay	0.06	11
	Coyote Creek	1.4	59
Dibenzothiophene	Coyote Creek	1.4	1 380

[α] Ca-montmorillonite clay, particle size <1 μm (obtained from Wyoming montmorillonite clay).
Coyote Creek, San Jose, California (eutrophic polluted stream).
Des Moines River, Iowa.
Searsville Pond, Woodside, California (eutrophic unpolluted pond).

For the above three natural sediments, no attempts were made to remove or kill the bacteria. Average sediment particle size <100 μm.

[β] Sorption includes any type of process whereby the substrate is physically or chemically bound to a solid surface.

Table 3-25. The sorption of some low-molecular weight PAHs on several types of particulate matter and sediments.

Compound	Sediment	$\mu g.L^{-1}$[α]	K_{ow}[β]	K_p[γ]	K_{oc}[δ]	Reference
Naphthalene	small pond sediment[ε]	31 700	2 300		1 300	Karickhoff et al. (1979)
2-Methylnaphthalene	small pond sediment	25 400	13 000		8 500	Karickhoff et al. (1979)
Anthracene	small pond sediment	73	35 000		26 000	Karickhoff et al. (1979)
Anthracene	organic particulates (autoclaved yeast cells)			25 000		Southworth (1979a)
Anthracene	wastewater treatment effluent (particulate organics)			≈2 500		Southworth (1979a)
Anthracene	natural sediment (inorganic clay fraction, 0.1-2.0 μm)			1 600		Southworth (1979a)
Anthracene	natural sediment (silt fraction, 5-10 μm)			≈100		Southworth (1979a)
9-Methylanthracene	small pond sediment	261	117 000		65 000	Karickhoff et al. (1979)
Phenanthrene	small pond sediment	1 290	37 000		23 000	Karickhoff et al. (1979)
Pyrene	small pond sediment	135	150 000		84 000	Karickhoff et al. (1979)
Naphthacene	small pond sediment	0.5	800 000		650 000	Karickhoff et al. (1979)

[α] Water solubilities taken from Mackay and Shiu (1977).

[β] K_{ow} = octanol-water partition coefficient.

[γ] K_p = sorption partition coefficient.

[δ] $K_{oc} = K_p/oc$, where oc is the fractional mass of organic carbon in the sediment.

[ε] Small pond sediment made up of coarse silt (20-50 μm). K_{oc}s are averages for isotherms run on Doe Run, Georgia (2.78% total organic carbon) and Hickory Hill, Georgia (3.27% total organic carbon) sediments.

3.4.1.2 Volatilization

The loss of more volatile hydrocarbons from water into the atmosphere is a well-known phenomenon, observed on numerous occasions in association with oil spills (cf. USNAS 1975). Spilled petroleum products are rendered less immediately harmful to biological systems by volatilization of more acutely toxic light-weight aromatic compounds such as benzenes and naphthalenes. Brown and Huffman (1976) examined waterborne hydrocarbons in open-sea tanker routes and noted reduced concentrations of lower-molecular-weight aromatic compounds. They suggested that aromatic hydrocarbons less than C_{15} (i.e. 1-, 2- and 3-ring compounds) were lost by volatilization or dispersion into the water column. They could not, however, explain the selective disappearance of heavier aromatic compounds ($> C_{15}$) using the same rationale. It was suggested that these hydrocarbons were lost through a mechanism of chemical or biological degradation or by sorption onto particulate matter followed by settling to the ocean floor.

Several experimental studies have shown that the loss from water of both low- and high-molecular-weight PAHs and HACs may be significant in specific circumstances. The rate of volatilization of a substance from a given body of water has been found to be dependent upon the physical-chemical properties of the substance (Liss 1973; MacKay and Wolkoff 1973; Liss and Slater 1974; MacKay and Leinonen 1975; MacKay *et al.* 1979) and such environmental factors as wind, water turbulence and temperature (Southworth 1979a). Henry's constant (the distribution coefficient representing the equilibrium distribution of a material between gaseous and liquid phases) was found to decrease with increasing molecular weight of PAHs. Using such constants and oxygen reaeration rates (the temperature-dependent rate at which oxygen from the atmosphere dissolves in oxygen-deficient waters), Smith *et al.* (1977, 1978) and Southworth (1979b) predicted the rate of volatilization of several PAHs and HACs from different aquatic ecosystems. In general, higher-molecular-weight PAHs, such as B[a]A and B[a]P, are relatively non-volatile, with half-lives extending beyond 100 h, while low-molecular-weight PAHs, such as naphthalene and anthracene, are more volatile, with half-lives less than 100 h. The rate of volatilization of PAHs was significantly influenced by both wind and current velocities (Southworth 1979b). For example, a 10-fold increase in either wind or current velocities resulted in a 4-fold increase in the volatilization rate of anthracene. A 10-fold increase in current velocity doubled the volatilization rate of B[a]A and B[a]P, while a 10-fold increase in wind velocity produced a 5-fold increase in volatilization rate.

3.4.1.3 Photo- and Chemical Oxidation

Much of the information that is available on the oxidative degradation of PAHs has been obtained from studies conducted in non-aqueous solutions (USNAS 1972); such studies have little relevance in

Table 3-26. Equilibrium sorption constants for selected PAHs, amino-PAHs, PAH-carboxylic acids, and nitrogen-heterocyclic compounds (after Means et al. 1979, 1980, 1982; Banwart et al. 1982).

Sediment/ Soil[α]	Percent Organic Content	Equilibrium Sorption Constants									
		Pyrene		7,12-Dimethylbenz[a]anthracene		3-Methylcholanthrene		Dibenz[a,h]anthracene		2-Aminoanthracene	
		$K_p(\times10^{-1})$	$K_{oc}(\times10^{-4})$	$K_p(\times10^{-2})$	$K_{oc}(\times10^{-5})$	$K_p(\times10^{-4})$	$K_{oc}(\times10^{-6})$	$K_p(\times10^{-4})$	$K_{oc}(\times10^{-6})$	$K_p(\times10^{-2})$	$K_{oc}(\times10^{-4})$
9[β]	0.11	7.1	6.5	10.3	9.3	0.3	2.4	0.3	2.3	1.0	9.4
8	0.15	10.1	6.7	6.1	4.1	0.2	1.5	0.2	1.2	0.8	5.3
14[β]	0.48	27.7	5.8	5.6	1.2	3.1	6.4	1.4	3.0	1.5	3.0
18	0.66	50.4	7.6	19.0	2.9	2.1	3.1	2.0	3.1	2.8	4.3
6	0.72	61.4	8.5	13.5	1.9	1.6	2.2	1.9	2.6	2.6	3.6
15	0.95	78.3	8.2	37.4	3.9	2.3	2.4	2.5	2.7	3.9	4.1
82	1.21	7.6	6.3	23.7	2.0	1.5	1.3	2.0	1.7	3.2	2.7
20[β]	1.30	72.3	6.0	16.2	1.2	1.6	1.2	0.7	0.6	4.6	3.5
26	1.48	99.4	6.7	37.4	2.5	3.7	2.5	4.0	2.7	6.9	4.7
22	1.67	80.6	4.8	26.8	1.6	2.1	1.3	4.0	2.4	5.0	3.0
21	1.88	111.9	6.0	55.8	3.0	2.5	1.3	5.6	3.0	5.3	2.0
4	2.07	106.5	5.1	26.5	1.3	3.0	1.5	3.5	1.7	3.3	1.6
5	2.28	115.5	5.1	52.1	2.3	0.8	0.4	1.8	0.8	3.0	1.3
23	2.38	104.3	4.4	67.8	2.8	1.7	0.7	1.9	0.8	8.6	3.7

Table 3-26. (Cont'd)

Sediment/ Soil[α]	Percent Organic Content	Equilibrium Sorption Constants									
		6-Aminochrysene		Anthracene-9-carboxylic acid		Acridine		Biquinoline		Dibenzocarbazole	
		K_p(x10^{-3})	K_{oc}(x10^{-5})	K_p	K_{oc}(x10^{-3})	K_p	K_{oc}(x10^{-4})	K_p	K_{oc}(x10^{-4})	K_p(x10^{-2})	K_{oc}(x10^{-6})
9[β]	0.11	0.7	6.2	2.8	2.6	34	3.1	61	5.6	10	0.9
8	0.15	0.6	3.8	1.8	1.2	33	2.2	57	3.8	31	2.1
14[β]	0.48	0.9	1.9	10.0	2.1	142	3.0	88	1.8	81	1.7
18	0.66	1.4	2.2	1.8	0.3	101	1.5	106	1.6	141	2.1
6	0.72	1.1	1.5	5.5	0.8	132	1.8	172	2.4	126	1.8
15	0.95	1.3	1.4	2.7	0.3	165	1.7	135	1.4	135	1.4
82	1.21	1.7	1.4	5.3	0.4	185	1.5	105	0.9	296	2.5
20[β]	1.30	0.9	0.7	13.3	1.0	193	1.5	93	0.7	155	1.2
26	1.48	1.7	1.1	7.5	0.5	213	1.4	180	1.2	216	1.5
22	1.67	1.5	0.9	5.6	0.3	92	0.6	181	1.1	180	1.1
21	1.88	2.6	1.4	6.5	0.3	207	1.1	216	1.2	170	0.9
4	2.07	3.1	1.5	5.5	0.3	334	1.62	220	1.1	258	1.3
5	2.28	4.0	1.7	8.0	0.4	278	1.2	164	0.7	146	0.6
23	2.38	3.9	1.6	10.0	0.4	287	1.2	243	1.0	139	0.6

[α] Soil and sediment samples were collected from sites along the Missouri, Ohio, Wabash, Illinois and Mississippi Rivers. For a complete characterization refer to Means et al. (1980).

[β] Soils; all others are sediments.

dilute aqueous systems. The most common photooxidation reaction of PAHs and HACs in non-aqueous solutions is the formation of endoperoxides (Southern and Waters 1960). Photolysis or thermal degradation of these endoperoxides yields a variety of products via dealkylation and ring cleavage. When, for steric reasons, an endoperoxide intermediate cannot be formed, quinones are produced (Masuda and Kuratsune 1966). McGinnes and Snoeyink (1974) tentatively identified the 1,6- and 6,12-quinones of B[a]P and the 7,12-quinone and a complex organic acid ($C_{18}H_{10}O_3$) of B[a]A when they photolyzed the parent hydrocarbons in aqueous solution. Smith et al. (1977, 1978) identified the 1,6-, 3,6- and 6,12-quinones of B[a]P upon photolysis in aqueous solution. It is believed that photooxidation reactions involving adsorbed PAHs do not proceed via the endoperoxide intermediate but instead produce quinones (Kortum and Braun 1960).

It has been suggested that there is an increased susceptibility to photodegradation when PAHs are adsorbed to particulate matter in aqueous systems (USNAS 1972; Neff 1979). However, this has not been demonstrated in experiments conducted to date. For example, the half-life of B[a]A increased from approximately 2.4 h in 20% acetone-water solution to approximately 24 h when B[a]A was dispersed in water as microspheres (1.25 μm diameter). The surface area-to-volume ratio of the particle appears to play a significant role in the rate of photooxidation, with smaller-sized PAH-containing particles being more quickly degraded than the larger-sized particles.

Whereas B[a]P in aqueous solution was degraded relatively rapidly, B[a]P that was dispersed in aqueous solution as microspheres (1.5 μm diameter) was degraded only slightly (McGinnes and Snoeyink 1974). Decomposition of B[a]P adsorbed to microspheres proceeded only to a depth of 0.2 μm with the resultant oxidation layer protecting the compound from further degradation. Similar auto-inhibitions appear to operate for PAHs adsorbed to atmospheric particulate matter (see Section 3.2.1.2). Such auto-inhibition was not observed for particulate B[a]A, which suggests that either the photolytic products were soluble and were easily removed from the surface of the particle, or that they were transparent to ultraviolet light.

The photooxidation of dissolved PAHs and some HACs appears to be relatively rapid under both laboratory and natural sunlight illumination, with half-lives ranging from approximately 30 minutes to 23 days, depending upon the compound and the photolytic conditions (Table 3-27); half-lives determined from photolyses in natural waters are longer by approximately 20-60% (Smith et al. 1978). In their study of the direct photochemical oxidation of various PAHs dissolved in water, Zepp and Schlotzhauer (1979) found that the photolytic reactions could be described by a first-order rate equation (Table 3-28). In general, quantum yields were in the range of 0.001-0.01. Photooxygenation involving singlet oxygen accounted for a negligible fraction of the observed photoreactions of PAHs dissolved in water.

Table 3-27. Photooxidation of some dissolved PAHs and HACs under natural sunlight conditions (after Smith et al. 1978; Southworth 1979a).

Compound	Rate constant (sec^{-1})	Half-life (h)
Anthracene	3.3×10^{-4}[α]	0.6
Benz[a]anthracene	3.3×10^{-4}[β]	0.6
Benzo[a]pyrene	3.6×10^{-4}[β]	0.5
Quinoline	3.5×10^{-7}[β]	548
Benzo[f]quinoline	3.7×10^{-4}[β]	0.5
Carbazole	1.9×10^{-4}[β]	1.0
7H-dibenzo[c,g]carbazole	5.5×10^{-4}[β]	0.4
Benzo[b]thiophene	5.7×10^{-6}[γ]	34
Dibenzothiophene	1.5×10^{-6}[γ]	128

[α] Anthracene in distilled water exposed to midday sunlight in midsummer at a latitude of 35°N (24-h photolysis for midsummer = 1.2×10^{-4} sec^{-1} and for midwinter = 4.0×10^{-5} sec^{-1}).

[β] Instantaneous rate constant for midday, midsummer at a latitude of 40°N.

[γ] 24-hour rate constant for midsummer at a latitude of 40°N.

Table 3-28. Kinetic data for direct photochemical degradation of PAHs in air-saturated water at 25°C (from Zepp and Schlotzhauer 1979).

Compound	Concentration (moles.L^{-1}) ($\times 10^7$)	Wavelength of Incident Light (nm)	Molar Absorptivity[α] ($g^{-1}.mole^{-1}.cm^{-1}$) ($\times 10^3$)	Disappearance Quantum Yield[γ] ($\times 10^3$)
Naphthalene	1.2×10^3	313	0.11 ± 0.005	15 ± 1
1-Methylnaphthalene	1.2×10^3	313	0.28 ± 0.01	18 ± 1
2-Methylnaphthalene	8.8×10^2	313	0.26 ± 0.01	5.3 ± 0.2
Phenanthrene	8.4	313	0.20 ± 0.01[β]	10 ± 1.6
Anthracene	2.3	366	2.1 ± 0.1	3.0 ± 0.2
9-Methylanthracene	3.1	366	9.9 ± 0.2	7.5 ± 0.5
9,10-Dimethylanthracene	1.3	366	4.0 ± 0.3	4.0 ± 0.4
Pyrene	3.9	313	8.8 ± 0.4	2.0 ± 0.3
Pyrene	3.9	366	0.19 ± 0.01	2.2 ± 0.3
Fluoranthene	6.6	313	3.8 ± 0.2	0.12 ± 0.01
Fluoranthene	6.6	366	3.5 ± 0.2	0.002 ± 0.002
Chrysene	8.2×10^{-2}	313	7.4 ± 0.2[β]	2.8 ± 0.7
Naphthalene	2.2×10^{-2}	436	6.1 ± 0.2[β]	13 ± 5

[α] Molar absorptivity in water.

[β] Obtained in 50% water-methanol.

[γ] Mean of triplicate determination.

This observation led the authors to speculate that the photolytic reactions may involve photoionization to form radical cation intermediates. Alternatively, singlet oxygen has been shown to be involved in the photodegradation of aromatic compounds dissolved in petroleum films (Larson et al. 1977).

In their study of mutagenic compounds in water, Suzuki et al. (1982), photolyzed naphthalene, anthracene and pyrene (20-25 $mg.L^{-1}$ as suspensions) in the presence of sodium nitrate (16.5% $mg.L^{-1}$ as NO_3-N) at 25°C for 3 hours. The reaction mixtures were found to be more mutagenic than the parent compounds; however, the reaction products were not isolated and hence, it is not possible to identify the causative agents.

It is suggested that the soluble and particulate material occurring in natural waters has an effect on the photodegradation of PAHs. Partitioning to sediment has a pronounced effect on the photolysis of higher-molecular-weight PAHs (Zepp and Schlotzhauer 1979); as the sorption partition coefficient increases for PAHs, the photolysis rates decrease (Table 3-29). Oliver et al. (1979) observed that sediments and clays suspended in the water column decreased the rate of photolysis by shielding the organic compounds from the available light. Alternatively, the presence of certain soluble compounds may enhance photolysis of PAHs. For example, the half-life of B[a]P in pond water decreased from 173 to 43 h in the presence of excess fulvic acid (Katz et al. 1979). The fulvic acid may have acted as a sensitizer or increased the water solubility of the B[a]P.

The free radical oxidation ($RO_2^{\bullet}$) of several PAHs and HACs was investigated by Smith et al. (1977, 1978) (see Table 3-30). Assuming a $RO_2^{\bullet}$ concentration of 10^{-9} M, the half-lives for B[a]A and B[a]P in air-saturated aqueous solutions were approximately 38h and 4.3d, respectively. Half-lives for quinolines, carbazoles and thiophenes were all very large, thus precluding free radical oxidation as an important removal mechanism in aquatic ecosystems.

In most natural waters, the absorption of light by dissolved and suspended matter would act to reduce the photolytic rate of PAHs and HACs and, in most cases, photolytic activity would be limited to the uppermost layers of waters (Southworth 1979a). In addition, photolytic activity will vary seasonally owing to changes in solar radiation, water temperature and dissolved oxygen levels.

3.4.2 BIOTIC CYCLING

3.4.2.1 Bioaccumulation

Evidence that PAHs accumulate in the tissues of aquatic organisms above those found in the surrounding water is available from

Table 3-29. Direct photolysis of PAHs in a 5-meter-deep inland water body[α] (from Zepp and Schlotzhauer 1979).

Compound	Sorption Partition Coefficient[β] K_p	Half-Life[γ] (days) No Partitioning[δ]	Half-Life[γ] (days) With Partitioning[δ,ε]
Naphthalene	4.7	550	550
1-Methylnaphthalene	61	180	190
2-Methylnaphthalene	61	410	440
Phenanthrene	180	59	69
Anthracene	160	4.5	5.2
9-Methylanthracene	550	0.8	1.2
Fluoranthrene	280	160	200
Pyrene	400	4.2	5.9
Benz[a]anthracene	1500	3.7	9.2
Chrysene	4200	13	68
Naphthacene	3800	0.2	1.0
Benzo[a]pyrene	3100	3.2	13

[α] Suspended sediment concentration, 20 $mg.L^{-1}$; diffuse attenuation coefficient, 11 m^{-1}.

[β] K_p computed from octanol-water partition coefficients.

[γ] Integrated over full summer day, latitude 40°N.

[δ] No partitioning assumes that PAHs are completely in the water column and the photolysis rates are affected only by light attenuation.

[ε] With partitioning describes rapid exchange between the top centimeter of the bottom sediment and the water column. This exchange could involve continual sedimentation and resuspension of the top layer of the bottom sediment.

Table 3-30. Free-radical oxidation of some PAHs and HACs in air-saturated water (after Smith et al. 1977, 1978).

Compound	Oxidation rate[α] (M^{-1} sec^{-1})	Half-life
Benz[a]anthracene	5.0×10^3	1.6 days
Benzo[a]pyrene	1.9×10^3	4.3 days
Quinoline	2.8	8 years
Benzo[b]quinoline	<2.8	>8 years
Carbazole	29	280 years
7H-dibenzo[c,g]carbazole	830	10 days
Benzo[b]thiophene	83	96 days
Dibenzothiophene	<7.5	>3.5 years

[α] Assumes $[RO_2^{\bullet}] = 10^{-9}$ M.

field studies and from studies using model ecosystems. Marine and freshwater organisms exposed to PAHs from point sources such as petroleum spills or chronic leakage, accumulated PAHs at the $\mu g.g^{-1}$ level (Disalvo et al. 1975; Grahl-Nielsen et al. 1978; Vanderkooy 1978; Mackie et al. 1980; Knutzen and Sortland 1982). Tissue levels in biota from remote or relatively unpolluted areas are found in the $ng.g^{-1}$ range (Murray et al. 1981; Brown and Pancirov 1979; Heit et al. 1980; Black et al. 1980).

The distribution of a PAH was studied in a model pond ecosystem by Giddings et al. (1977). ^{14}C-anthracene added to the system disappeared rapidly during the first two weeks and was found in increasing concentrations in sediments, vegetation and animals. Measured levels of total extractable ^{14}C in the various biota and sediments, relative to its concentration in water (bioconcentration factor), are presented in Table 3-31. Sampling was conducted over a period of 70-84 days after the addition of the labeled PAH and all organisms were found to accumulate activity to about 10^3 times its concentration in water. This is in agreement with the bioconcentration factor of 1190 which was calculated by Southworth et al. (1978a) for anthracene in Daphnia pulex. Similar studies were conducted on the distribution of B[a]P levels in water, sediment, plants, plankton, molluscs and fish from water reservoirs receiving treated municipal effluents (Il'nitsky et al. 1979b). B[a]P was found to be elevated in sediment and biota at 10^2-10^4 times the level found in water (in order of decreasing levels: bottom sediment > water plants > fish >>water). However, methods of analysis for B[a]P in this study were not discussed by the authors.

Results of studies on the distribution of PAHs from a creosote point source in a river system in Michigan for a number of aquatic species are presented in Table 3-32 (Black et al. 1980). The wet weight concentrations ($ng.g^{-1}$) of phenanthrene, benzanthracene and B[a]P in major indigeneous fish and invertebrate species follow the order: sediments > insects > crayfish > lampreys > trout > white suckers.

Total PAH levels (12 compounds measured) in sediment near the outflow from a steel industry/coke oven complex at Sydney, Nova Scotia were found to be as high as 2830 $\mu g.g^{-1}$ (dry weight) (EPS 1982). This diminished to 40-50 $\mu g.g^{-1}$ at sites 8 km away; however, even at the mouth of the harbor 16 km from the source, levels exceeded 7 $\mu g.g^{-1}$. One of the PAHs measured, B[a]P, ranged from 108.5 $\mu g.g^{-1}$ near the outfall to 0.37 $\mu g.g^{-1}$ in a separate arm of the harbor and dropped to 0.026 $\mu g.g^{-1}$ approximately 16 km from the source. Corresponding PAH levels in mussels, Mytilus edulis and Volsella modiolus collected from Sydney Harbour, were 4.12 $\mu g.g^{-1}$ (wet weight) near the source, which dropped to 0.471 $\mu g.g^{-1}$ approximately 16 km from the source (a drop of one order of magnitude as opposed to a 400-fold drop in sediments). Benzo[a]pyrene ranged from 0.006 $\mu g.g^{-1}$ (wet) to 0.28 $\mu g.g^{-1}$ in mussels collected from the harbor (EPS 1982). Levels of total PAH and

Table 3-31. Bioaccumulation of anthracene through various trophic levels (simulated pond conditions; 70-84 days) (from Giddings *et al.* 1977).

	Bioaccumulation factor
Water	1
Sediment	
Upper 5 cm	12 - 27
Upper 2 cm	200
Plants	
Periphytes	600 - 700
Elodea	800 - 900
Algae	700 - 1000
Animals	
Zooplankton	400 - 900
Water mites	1000 - 1500
Snails	1000 - 1900
Snail eggs	700

Table 3-32. Concentrations of 3 PAHs ($ng.g^{-1}$ wet weight) in sediments and biota of the Hersey River, upstream (control) and 20 km downstream from a creosote point source (from Black *et al.* 1980).

	Phenanthrene		Benz[a]anthracene		Benzo[a]pyrene	
	Upstream	Downstream	Upstream	Downstream	Upstream	Downstream
Sediment	16	4 098	0.3	3504	0.3	1194
Insects	42	5 489	7	2893	1	725
Crayfish	6	447	2	40	0.6	8
Lamprey	35	15 313	ND	20	0.8	1
Trout	2	38	0.2	0.2	0.04	0.07
Sucker	4	28	0.1	0.1	0.05	0.08

B[a]P in the tail muscle and hepatopancreas were one order of magnitude lower in lobsters (Homarus americanus) taken 10 km away from the outfall than those near the outfall (Table 3-33).

An important aspect of the environmental fate of PAHs is the extent to which they are accumulated in aquatic organisms. Of major concern is the possibility that PAHs accumulate at tissue levels that are toxic. This has implications for human as well as animal health since exposure to PAHs would result from consumption of aquatic organisms with high levels of PAHs in tissue.

In biota, uptake processes for non-polar organic compounds such as PAHs are thought to be related to the chemical's physical-chemical properties. The hydrophobicity of PAHs is recognized as the driving force for partitioning of PAHs between aqueous and lipid phases (Bruggeman et al. 1982). Mackay (1982) has suggested that a directly proportional relationship exists between the bioconcentration factor and the octanol-water partition coefficient (K_{ow}), a parameter frequently used as an indicator of the tendency of compounds to distribute between water and biological tissue across cell membranes. For most aquatic organisms, including plants and animals (both invertebrate and vertebrate), uptake of PAHs occurs directly through the integument (Metcalf 1977) or, in more complex organisms, from water to blood through gills and from blood to tissues. Assimilation of PAHs through the gut, from ingested material, is another route of uptake.

The extent to which a compound is bioaccumulated by aquatic organisms, relative to the surrounding media (most often water), is called the bioconcentration factor (BCF) and reflects an equilibrium between the competing processes of uptake, and depuration and metabolism. Measurement of the BCF for a particular compound can be made by exposing organisms for a period long enough to allow residue detection at steady-state equilibrium. If the time necessary to reach steady-state is too long, the BCF can be calculated from rate constants derived from a given kinetic model. Species differences in the metabolic handling of PAHs are an important factor in determining differences in steady-state concentrations and apparent bioaccumulation factors of PAHs. Metabolic processes in relation to bioaccumulation of PAHs are discussed more fully in Section 3.4.2.2.

Rates of uptake and elimination, and equilibrium constants (BCFs) for the partitioning of 7 representative PAHs and 3 azaarenes between water and the zooplankter Daphnia pulex were measured in laboratory studies (Southworth et al. 1978a, b). Uptake and elimination were assumed to be first-order processes, dependent on the concentration of the compound in water or in the organism, respectively. Values of the uptake and elimination rate constants (Table 3-34) are high, indicating rapid establishment of equilibrium between Daphnia and water for each compound. Although uptake rates did not greatly differ for the PAHs and azaarenes tested, there was a marked difference in their

Table 3-33. Levels of total PAHs and benzo[a]pyrene (in brackets) in 2 groups of lobsters collected from Sydney Harbour, Nova Scotia near the outflow of a steel industry/coke oven complex. Values represent wet weight measurements in tissue, in units of $\mu g.g^{-1}$ (from Sirota et al. 1982).

	Close to source	10 km away
muscle	2.7/2.9 (0.04/0.02)	0.050/0.053 (0.002/0.0022)
hepatopancreas	88.1/57.3 (1.0/2.0)	8.7/10.7 (0.226/0.253)

Table 3-34. Octanol-water partition coefficients (P), uptake (k_1) and excretion (k_2) rate constants, and bioconcentration factors (BCF) for PAHs (Southworth *et al.* 1978a) and azaarenes (Southworth *et al.* 1978b) in *Daphnia pulex*.

PAH/azaarene	log P	$k_1(h^{-1})$	$k_2(h^{-1})$	BCF
Naphthalene	3.30	197	1.67	118
Phenanthrene	4.45	203	0.543	374
Anthracene	4.45	702	0.589	1190
9-Methylanthracene	5.12	561	0.144	3900
Pyrene	4.90	1130	0.343	3280
Benz[a]anthracene	5.60	669	0.144	4650
Perylene	6.06	752	0.139	5400
Isoquinoline	1.82	82	34.2	2.41
Acridine	3.30	109	3.68	29.6
Benz[a]acridine	4.45	208	0.59	352

tendency to accumulate in daphnid tissues, which was due mainly to differences in the elimination rates for each compound. The equilibrium BCFs (Table 3-34) were shown to be positively correlated with the octanol-water partition coefficients (K_{ow}) for each compound. K_{ow} is thought to best approximate the partitioning of compounds from the aqueous environment into animal lipids and is dependent on chemical structure (Leo 1975). The equation for the correlation derived between K_{ow} and BCF values for the 10 PAHs can be used to predict the BCF factor in Daphnia of a PAH, if its K_{ow} is known.

The observed bioconcentration of several azaarenes in a more developed organism, the fathead minnow (Pimephales promelas), did not agree with predicted values based on octanol-water partition coefficients and BCFs (Southworth et al. 1980). It was found that metabolic degradation of azaarenes in the fish was making a substantial contribution to their elimination from the minnow, thus decreasing the potential for bioaccumulation. The authors concluded that Daphnia was a better organism than fish for predicting a compound's tendency to bioconcentrate based on correlations with its physical properties. In fish, actual measurement was necessary to establish the degree of concentration. This finding was in agreement with the results of Leversee et al. (1981) who calculated the bioconcentration of B[a]P in Daphnia, chironomids and bluegill sunfish (Lepomis macrochirus). Because of active biotransformation, the measured BCF was an order of magnitude less in sunfish and chironomids than would have been predicted from uptake and depuration rate constants. Herbes and Risi (1978) concluded that in Daphnia pulex, metabolism contributed little to decreasing the body burden of PAHs and that, in general, the metabolic alteration of PAHs by zooplankton may be more significant as a mechanism for removal of PAHs from natural waters than as a mechanism preventing biomagnification of PAHs along the food chain.

Studies on transport processes for 4 PAH compounds have been conducted with oysters (Crassostrea virginica) (Lee et al. 1978). Since a two-day exposure period was not considered sufficient to establish an equilibrium between the uptake and elimination processes, equilibrium BCFs for the PAH were estimated from the ratio of the uptake and elimination rate constants (Table 3-35). For the measurement of elimination rate constants, oysters were transferred to clean water in order to depurate accumulated PAHs. Based on these experiments, half-lives for the 4 PAHs were calculated. These data suggest that the higher-molecular-weight PAHs are more persistent in oyster tissues than are PAHs of lower molecular weight.

In a study in which mussels (Mytilus edulis) from a site contaminated with PAHs were moved to a clean site, B[a]P was depurated from tissue levels of 23 $\mu g.g^{-1}$ (wet or dry weight not specified) to background levels (approximately 1 $\mu g.kg^{-1}$) with a half-life of 8-10 d (Mix et al. 1981). Release of B[a]P from tissues followed a biphasic mode with an initially rapid turnover of B[a]P and then a long, slow

Table 3-35. Uptake (k_1) and excretion (k_2) rate constants of PAHs for oysters (Crassostrea virginica) in 2-day uptake studies (from Lee et al. 1978).

PAH	$k_1(h^{-1})$	$k_2(h^{-1})$	$t_{\frac{1}{2}}(h)$	BCF(k_1/k_2)
Anthracene	11.2	0.009 63	72	1160
Fluoranthene	16.6	0.005 78	120	2860
Benz[a]anthracene	11.9	0.003 21	216	3700
Benzo[a]pyrene	4.09	0.001 60	432	2560

phase of release. This biphasic depuration suggested to the authors that PAHs are stored in two compartments within the shellfish.

Uptake and depuration kinetics of B[a]P were determined for the larval midge (Chironomus riparium), a benthic organism burrowing in freshwater sediments. A bioconcentration value of 200 based on B[a]P analysis was observed (Leversee et al. 1982). This was lower than the BCF of 650 determined from the measurement of steady-state ^{14}C-B[a]P; biotransformation of B[a]P accounted for the difference between measurement of ^{14}C-label and the actual B[a]P measurement.

Uptake and disposition of PAHs have been measured in vertebrate fish using ^{3}H- and ^{14}C-labelled compounds in surrounding water (Lee et al. 1972b), administered by intraperitoneal (i.p.) injection (Roubal et al. 1977; Hose et al. 1981), and adsorbed to food (Roubal et al. 1977; Whittle et al. 1977). Results from feeding experiments using Coho salmon (Oncorhynchus kisutch) (Roubal et al. 1977) indicated that substantially more ^{14}C activity from anthracene was accumulated in the tissues than from naphthalene (^{14}C activity was expected to be associated with the unchanged compound and its metabolic products), even when equivalent molar amounts were administered. Also, anthracene and its products were generally more persistent than naphthalene and its products. The highest levels of ^{14}C-activity for each ingested PAH tested were found in brain and liver, a result substantiated by injection studies. Accumulation of PAHs in tissues was not intercomparable between feeding and intraperitoneal injection studies. In feeding studies by Whittle et al. (1977), B[a]P was mainly associated with tissues of the stomach and gut (98.4% of ^{14}C-activity; 81.6% for stomach alone). The results seemed to imply strong adsorption or binding to the stomach wall, but comparatively little absorption across it. This is in contrast to the results of Lee et al. (1982) in which absorption of ^{3}H-B[a]P and ^{14}C-naphthalene from aquarium water (across the gills) was rapid and could be detected in most tissues within a few minutes. In the first hour of the uptake experiments the liver, gut and gill tissues contained most of the hydrocarbon. Longer periods of exposure resulted in accumulation of hydrocarbon by the fish and especially by the gall bladder. When fish were placed in clean seawater, radioactivity was lost, naphthalene and its metabolites being more quickly depurated than B[a]P.

Black et al. (1980) have related PAH accumulation to lipid content in vertebrate fish. When comparing white sucker (Catastomus commersoni) and brown trout (Salmo trutta) populations from a river with sediments heavily contaminated with PAHs from a creosote source upstream, they noted higher levels of PAHs in trout even though the suckers were bottom-feeders. Measurements indicated 2.11% and 0.18% lipid in muscle of brown trout and white sucker respectively; the authors suggested that differences in tissue lipid content could provide a basis for the observed results.

Hose et al. (1981) investigated the uptake of ^{3}H-B[a]P by the gonads and gametes of sexually mature English sole (Parophys vetulis). From 0.53 to 3.69% of the administered dose was found in the ovary 24 h after i.p. injection, which was lower than the percentage of total body weight contributed by this organ. Similar results were obtained for testes. Most of the radioactivity was due to the parent compound (ovary-98%; testes-97%) although small amounts of polar metabolites were also present. Since the levels of B[a]P and its metabolites in ripe eggs and semen were several times greater than the levels in the gonad itself (averaging 30 $\mu g.g^{-1}$ (wet weight) ovary, 160 $\mu g.g^{-1}$ eggs; 25 $\mu g.g^{-1}$ testes, 165 $\mu g.g^{-1}$ semen), it appeared that these compounds accumulated within the developing gametes.

Kühnhold and Busch (1978) performed studies on the uptake of B[a]P by Atlantic salmon eggs (Salmo salar) (stage of development not indicated) at 12, 72, and 168 h after addition of the PAH to their medium. Although partitioning of B[a]P between salmon eggs and medium took longer to reach a steady state than did naphthalene (a diaromatic compound), B[a]P reached a greater equilibrium concentration ($BCF_{B[a]P}$- 70.7; BCF_{Naph} - 43.9).

Preliminary studies with sulfur heterocyclic aromatic compounds (PASH), which are components of coal liquids and air particulates, indicate that they were concentrated in Black River and Potomac River fish samples at high levels relative to PAHs (Vassilaros et al. 1982a). In a coal tar PAH fraction, the ratio of phenanthrene to dibenzothiophene was approximately 15:1, whereas the average ratio from four different fish samples from the Black River was 9:1 and from corresponding sediment samples, 19:1. An analysis of the physical-chemical properties of the compounds revealed that while the octanol-water partition coefficients of several PASHs and analogous PAHs were practically identical, the aqueous solubilities of the PASHs were higher. This would result in greater bioavailability of PASHs, which is reflected in the relative amounts of PASHs and PAHs detected in fish tissue (Vassilaros et al. 1982b).

Mallard drakes (Anas platyrhynchos) dosed with South Louisiana crude oil accumulated petroleum hydrocarbons in every tissue analyzed, with skin and underlying adipose tissue qualititatively showing the greatest extent of accumulation (Lawler et al. 1978). In skin and other tissues, 2- and 3-ring PAHs (naphthalene, alkylnaphthalenes, phenanthrene) were accumulated in preference to benzenes and alkylbenzenes relative to their occurrence in crude oil. Aromatic hydrocarbons were also found in eggs laid by mallard ducks fed mash containing 25 000 $\mu g.g^{-1}$ South Louisiana crude oil (Belisle et al. 1981). In this study, naphthalene and 1-methylnaphthalene were the most abundant aromatics in treated eggs; larger molecular weight PAHs, fluorene and phenanthrene were also detected.

The uptake of PAHs from food relative to uptake from water, has been compared in larvae of the hard clam, Mercenaria mercenaria

(Dobroski and Epifanio 1980) and in the fathead minnow, Pimephales promelas (Southworth 1979a; Southworth et al. 1979b). Transfer of B[a]P from an algal food source containing 42.2 $\mu g.g^{-1}$ dry weight B[a]P to the larvae of Mercenaria mercenaria was measured as occurring at a rate of 2.1 $\mu g.g^{-1}.d^{-1}$. The rate of direct uptake of B[a]P from seawater containing 30 $\mu g.L^{-1}$ was calculated for the clam Rangea cuneata by Neff and Anderson (1975) to be 6 $\mu g.g^{-1}.d^{-1}$. Extrapolating to the seawater concentration of B[a]P used in this study, 10 $\mu g.L^{-1}$ (since B[a]P is relatively insoluble in water, a nontoxic carrier solvent, polyethylene glycol was used), the rate of direct uptake from seawater by clam larvae would be 2.0 $\mu g.g^{-1}.d^{-1}$ compared with the measured rate of trophic transfer, 2.1 $\mu g.g^{-1}.d^{-1}$. This suggests that uptake from both water and food contribute significantly to the accumulation of B[a]P in filter-feeding bivalves. Southworth (1979a) and Southworth et al. (1979b) compared uptake rates of anthracene and acridine by the fathead minnow from a food source (Daphnia pulex) and from water. For a 200-g minnow in a solution of 1 $\mu g.L^{-1}$ anthracene, direct uptake from solution proceeded at a rate of 6.2×10^{-3} μg anthracene.h^{-1}; ingestion of 10% of their live weight per day of Daphnia (equilibrated in the same anthracene solution) resulted in uptake of 1.0×10^{-3} μg anthracene.h^{-1}. It would therefore be necessary for minnows to ingest 60% of their live weight in Daphnia for the two processes to be of equal importance. The uptake rates of acridine from water and from Daphnia were calculated from experimentally determined concentration factors and uptake/elimination rates of Pimephales promelas. Assuming an acridine concentration in water of 100 $\mu g.L^{-1}$ and an ingestion rate of 5% of live weight per day, direct uptake from water accounted for 98% of acridine uptake whereas uptake from food accounted for only 1%.

The bioavailability of PAHs to aquatic organisms is strongly influenced by their association with particulate material. The presence of sorptive yeast particles greatly decreased the uptake rate and bioconcentration of B[a]P and anthracene by Daphnia magna (McCarthy 1981). Roesijadi et al. (1978) and Anderson et al. (1978) have compared the uptake of several PAHs by the deposit-feeding clam, Macoma inquinata, from oil-contaminated detritus and from seawater. The data in Table 3-36 show that the clams concentrated PAHs from seawater to a considerably higher degree than they did from sediment. Sediment magnification factors were typically less than 0.1, while seawater magnification factors ranged from 10 to greater than 10^3. In addition, seawater magnification factors increased with increasing size of the PAHs but total accumulation of the PAHs by the clams was of the same order of magnitude, whether from sediment or seawater. This led the authors to speculate that the observed uptake of PAHs by clams from sediments may be taking place from PAHs present in interstitial water rather than from what is actually sorbed to sediment particles.

As mentioned in Section 3.4.1.1, PAHs are sparingly soluble in fresh- and seawater and are found mostly adsorbed to particulates; however, an exchange equilibrium exists which means that some portion,

Table 3-36. A comparison of PAH concentrations in clams (Macoma inquinata) exposed to sediment containing 2000 $\mu g.g^{-1}$ crude oil spiked with 10 μC of the hydrocarbon indicated. Clams were suspended in water or embedded in sediment (from Roesijadi et al. 1978).

PAH	Concentration in clam tissue ($\mu g.g^{-1}$)		Concentration in		BCF	
	Sediment	Water	Sediment ($\mu g.g^{-1}$)	Water ($\mu g.mL^{-1}$)	Sediment	Water
Phenanthrene	.096	.038	.49	3.7	.20	10
Chrysene	.308	.297	8.37	.43	.04	694
Dimethylbenz[a]anthracene	.297	.856	4.63	.63	.06	1349
Benzo[a]pyrene	.059	.037	.64	.043	.09	861

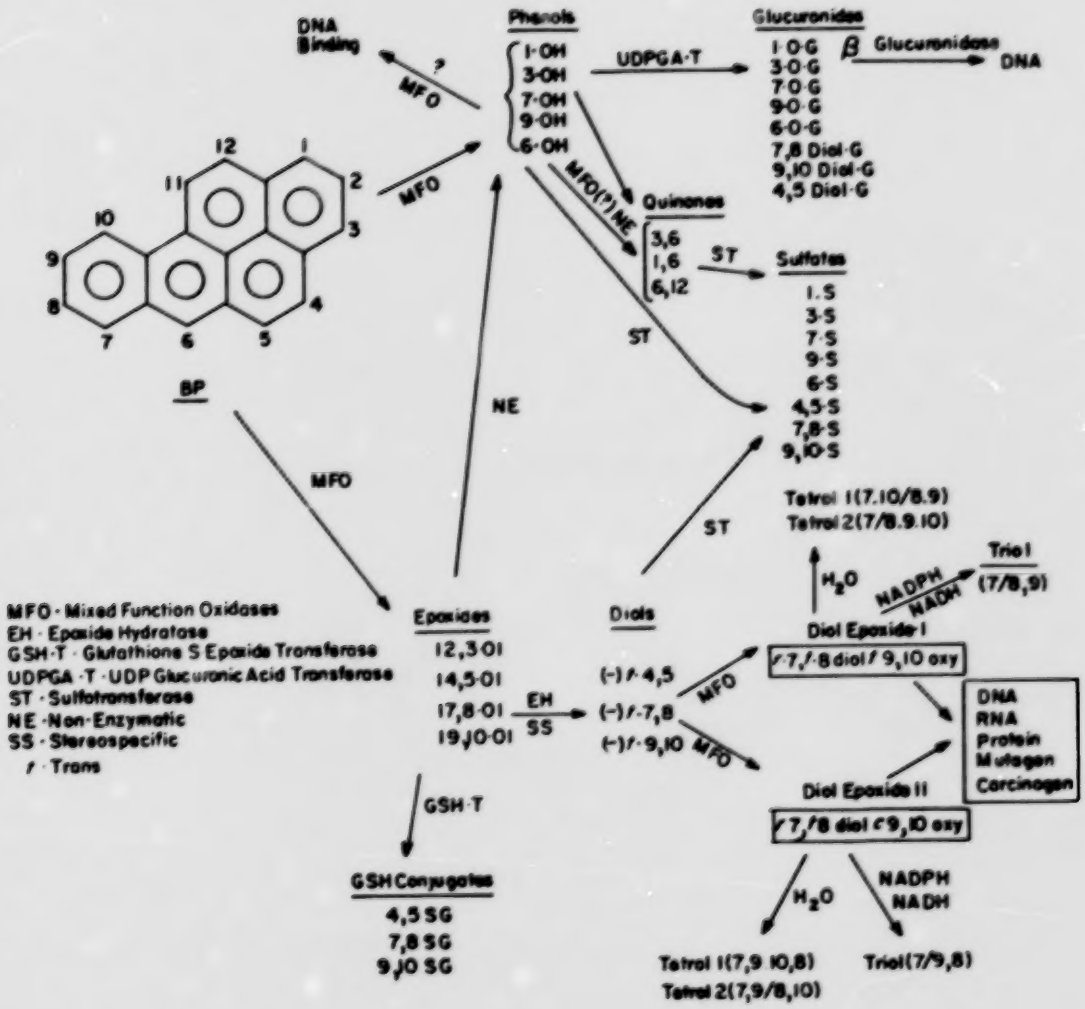

Figure 3-1. Metabolism and activation of benzo[a]pyrene in mammals (from Gelboin 1980).

even of the high-molecular-weight compounds, exists in solution. Since octanol-water partitioning provides a good estimate of particulate-water partitioning (Means et al. 1979), the low-molecular-weight PAHs with low K_{ow} would be less firmly adsorbed and would be in higher concentration in interstitial water than higher-molecular-weight compounds with higher K_{ow} values. Support for the idea that sorption processes can determine bioavailability is found in the results of Dunn (1980) who showed that as the molecular weight and hydrophobicity of PAHs increased, there was a general trend toward lower levels in mussels relative to levels in sediments.

3.4.2.2 Metabolism

Some aquatic invertebrate and vertebrate species possess enzymatic systems capable of metabolizing PAHs. Evidence for a mixed-function oxidase (MFO) system similar to that in mammals has been found in a number of aquatic species (Table 3-37). These enzymes, which are often referred to as phase I enzymes, are believed to be responsible for virtually all primary (oxidative) products of aromatic hydrocarbon metabolism (Malins 1977). The process whereby an oxygen is introduced into the aromatic ring structure is NADPH-dependent and involves an electron transport system that includes the so-called P_{450} network of cytochromes. The distribution of tissue activity may differ in various species; for instance, metabolizing ability predominates in the liver of fish, the hepatopancreas of crustaceans and molluscs, and the lower intestine of polychaete worms.

Further primary metabolism of PAHs results in the formation of quinone, phenol and trans-dihydrodiol derivatives. Since these metabolites are more water-soluble than are the parent compounds, lipid-water partitioning does not favor their accumulation in tissue lipids and they would be expected to have a faster rate of elimination from animal tissues. The term aryl hydrocarbon hydroxylases (AHH) is used to denote enzyme activity that catalyzes reactions such as the formation of 3-hydroxybenzo[a]pyrene from B[a]P. The many types of reactions involved in the biotransformation of B[a]P in mammalian systems are illustrated in Figure 3-1 (Gelboin 1980). Both phase II conjugating enzymes and phase I reactions are presented in detail.

There is limited information available on the types of PAH metabolites formed by aquatic organisms; most studies have dealt with the hepatic metabolism of B[a]P by a few fish species (Stegeman 1981). The pattern of dihydrodiol, quinone and phenol derivatives formed by fish appears to be qualitatively similar to metabolite profiles produced in mammalian systems (Table 3-38), but the various types of primary oxidative metabolites produced by representative species of various invertebrate phyla have been studied to a lesser degree. The limited studies on crabs (Callinectes sapidus) (Singer et al. 1980), lobsters (Panulirus argus) (James and Little 1980) and barnacles (Balanus

Table 3-37. The presence and inducibility of aryl hydrocarbon hydroxylase in some aquatic animal species (adapted from Uthe 1979). ++ indicates high activity compared with that of other species; +, presence of enzyme activity; -, no significant activity; ? not studied.

Species	Basal activity	Inducibility	Reference
Zooplankton			Walters et al. (1979)
(Calanus finmarchius;	+		
C. helgolandicus)	+	+	
Polychaete worm (Capitella capitata)	+	+	Lee (1976); Lee and Singer (1980)
(Nereis succinea)	+	+	Lee (1976); Lee and Singer (1980)
(N. virens)	+	+	Lee (1976); Lee and Singer (1980)
Lugworm (Arenicola sp.)	-	-	Payne and May (1979)
Sea anemone (Metridium sp.)	-	-	Payne (1977)
Snail (Littorina littorea)	+	-	Payne and May (1979)
Sea urchin (Strongylocentrotus drobachiensis)	+	-	Payne and May (1979)
Sea star (Asterias sp.)	+	-	Payne and May (1979)
Blue Mussel (Mytilus edulis)	-	-	Vandermeulen and Penrose (1978)
Freshwater clam (Anodonta sp.)	-	-	Payne and May (1979)
Scallop (Placopecten sp.)	-	-	Payne (1977)
Soft-shell clam (Mya arenaria)	-	-	Vandermeulen and Penrose (1978)
European oyster (Ostrea edulis)	-	-	Vandermeulen and Penrose (1978)
Oyster (Crassostrea virginica)	+	+	Anderson (1978)
Amphipod (Gammarus sp.)	-	-	Payne (1977)
Rock crab (Cancer irroratus)	-,+	-	Payne (1977); Philpot et al. (1977)
Blue crab (Callinectes sapidus)	-,+	?	Philpot et al. (1977); Lee et al. (1976)
Brine shrimp (Artemia salina)	-	?	Payne (1977)
Lobster (Homarus americanus)	-,+	-	Payne (1977); Philpot et al. (1977)
Spiny lobster (Panolirus argus)	-	-	Philpot et al. (1977)
Crayfish (Cambarus sp.)	+	?	Khan et al. (1972)
Squid (Illex illecebrosus)	+	?	Malins (1977)
Dogfish (Squalus acanthias)	+	+	James and Bend (1980)
Nurse shark (Ginglymostoma irratum)	+	?	James et al. (1979b)

Table 3-37. (Cont'd)

Species	Basal activity	Inducibility	Reference
Large skate (*Raja ocellata*)	+	+	James and Bend (1980)
Little skate (*Raja erinacea*)	+	?	James and Bend (1980)
Thorny skate (*Raja radiata*)	+	?	Philpot *et al.* (1977)
Stingray (*Dasyatis sabina*)	+	+	James and Bend (1980)
Mummichog (*Fundulus heteroclitus*)	++	+	Stegeman (1978); James *et al.* (1979b)
Winter flounder (*Pseudopleuronectes americanus*)	+	+	Bend *et al.* (1979)
Southern flounder (*Paralichtheyes lethostigma*)	+	+	James and Bend (1980)
Eel (*Angilla rostrata*)	+	+	Nava and Engelhardt (1980)
Sheepshead (*Archosargus probatocephalus*)	++	+	James and Bend (1980)
Drum (*Pongonias cromis*)	+	?	Philpot *et al.* (1977)
Rainbow trout (*Salmo gairdneri*)	++	+	Gernart and Carlson (1978); Förlin (1980)
Brown trout (*Salmo trutta*)	+	+	Anokas *et al.* (1975)
Brook trout (*Salvelinus fontinalis*)	+	+	Payne (1977); Vandermeulen and Penrose (1978)
Capelin (*Mallotos villosus*)	+	+	Payne (1977)
Cunner (*Tautogolabrus adspersus*)	+	+	Payne (1977)
Herring (*Chipea harengus*)	+	?	Payne (1977)
Cod (*Gadus morhua*)	+	+	Payne and Fancey (1982)
Sculpin (*Myoxocephalus* sp.)	+	+	Payne and Fancey (1982)
Bluegill (*Lepomis macrochiros*)	+	?	Malins (1977)
Coho salmon (*Onchorhynchus kisutch*)	+	?	Malins (1977); Schnell *et al.* (1980)
Scup (*Stenotomus versicolor*)	+	?	Stegeman *et al.* (1979)

[a] ++ indicates high activity compared with that of other species; +, presence of enzyme activity; -, no significant activity; ?, not studied.

Table 3-38. Microsomal metabolites of benzo[a]pyrene[α] (from Stegeman 1981).

Species	Treatment	Total metabolites (%)						Total activity (pmol $min^{-1}.mg^{-1}$)
		9,10-Diol	4,5-Diol	7,8-Diol	Quinones	Phenol I	Phenol II	
Fish								
Little skate[β]	Control	9	4	15	4	18	50	44
Little skate	DBA	11	1	13	26	17	32	740
Scup[β,δ]	Control	22	ND	33	27	3	14	1061
Scup	3-MC	6	ND	12	16	11	55	2174
Sheepshead[γ]	Control	22	5	21	15	12	12	503
Sheepshead	3-MC	12	2	22	11	9	19	2750
Southern flounder[γ]	Control	26	3	27	12	12	12	90
Southern flounder	3-MC	26	2	32	9	3	17	810
Fundulus heteroclitus[δ]	None	19	1	20	27	5	29	314
Trout S. trutta[ε]	None	22	1	27	14	2	33	260
Fundulus parvipinnis[ζ]	None	18	3	20	8	7	45	134
Crustacean								
Barnacle[η]	None	7	ND	14	1	19	58	13
Mammal								
Rat[θ]	Control	8	6	4	34	13	35	1156
Rat	PB	7	23	3	28	8	30	1393
Rat	3-MC	18	6	14	19	6	36	4970

[α] Bend et al. 1979;

[β] Stegeman and Woodin 1980;

[γ] Stegeman 1983, Personal communication.

[δ] Stegeman 1983, Personal communication.

[ε] Stegeman 1983, Personal communication.

[ζ] Anokas et al. 1979;

[η] Stegeman and Kaplan 1981;

[θ] Pezzuto et al. 1978.

All results presented were obtained by HPLC analysis of [^{14}C]- or [^{3}H]BP metabolites. Abbreviations: DBA, 1,2,3,4-dibenzanthracene; 3-MC, 3-methylcholanthrene; PB, phenobarbital; ND, not detected. Phenols I and II refer to compounds eluting with 9-OH-BP and 3-OH-BP, respectively.

eburneus) (Stegeman and Kaplan 1981) have indicated differences in the relative amounts of phenols and diols formed. However, no general statement on interspecies differences can be made until variables such as sex, age, season and the presence of natural or artificial inducers in the surrounding environment have been further elucidated. In reference to various conjugating enzymes, it appears that fish may be similar to mammals in having the potential to produce various polar derivatives including glucuronides, glycosides and mercapturates excreted in the bile or urine. Sulfate conjugation may also be important in aquatic vertebrates and invertebrates but the data base on phase II enzymes is quite limited.

Earlier in vivo and in vitro studies with bivalve molluscs failed to demonstrate PAH metabolism. Negative results were reported by Lee et al. (1972a) who failed to detect metabolism in mussels injected with B[a]P and by Payne (1977) and Payne and May (1979) who did not find evidence for metabolism in any of a number of aromatic and heteroaromatic compounds incubated with tissue preparations of fresh and salt-water bivalves. Similar observations were reported by Vandermeulen and Penrose (1978) who assayed whole animal homogenates of soft shell clams and oysters. However, Anderson (1977) reported the presence of low AHH activity levels in the digestive gland of oysters. Anderson employed a radiometric procedure and assayed the 'total' amount of ^{14}C-metabolites formed in microsomal preparations while the fluorometric assay used in earlier in vitro studies preferentially detected the presence of phenols, with 3-OH-B[a]P generally being the major metabolite formed. Recent studies by Stegeman (1980) and Payne et al. (1983) have also demonstrated low activity levels in various species of marine and freshwater bivalves. Stegeman has shown that the activity in two species of mussels was quite low when measured with the fluorescence assay - less than 1 pmol 3-OH-B[a]P.min^{-1}.mg^{-1} protein. In contrast, activity found in tissue preparations from fish can be 1-2 orders of magnitude higher. Thus both in vivo and in vitro studies indicate that bivalves have a limited capacity to transform PAH compounds. It is worth noting however, that MFO catalytic activity could possibly be improved with the use of various "stabilization" buffers similar to those developed for a few crustacean species (Lee et al. 1981).

MFO enzyme activities have been demonstrated in tissue preparations of a few species of crustaceans including crabs and lobsters and more recently, copepods (Walters et al. 1979). MFO can also be assumed to be present in other marine invertebrates where in vivo studies have shown PAH metabolism. Enzyme levels first reported in crustacean tissues were also quite low and it has been suggested that such low activity may be due to the presence of endogenous inhibitors or degradative enzymes. James et al. (1979b) reported that the digestive gland of spiny lobster had the highest specific cytochrome P-450 content of all species studied (compared with teleost and elasmobranch fish), whereas in vitro mixed-function oxygenase (MFO) activity was two orders

of magnitude lower. Lee et al. (1981) have improved the detection of MFO activity in crustacean tissues, but there is insufficient information available to make general comparisons with activity levels found in fish.

Instances of high levels of PAHs found in lobsters indicate a limited detoxification potential that may be MFO-related. Dunn and Fee (1979) noted high levels (281 $ng.g^{-1}$) of B[a]P in the edible tissue of lobster retained in creosoted pounds; similar very high levels of PAHs (up to 88.1 $\mu g.g^{-1}$) have been documented by Sirota et al. (1982) in lobster taken near a coking oven complex in Nova Scotia. Although many anatomical and physiological parameters may influence depuration rate, studies with both fish (e.g. Varanasi and Gmur 1981) and bird (Peakall et al. 1980) species known to contain relatively high MFO activity levels depurate hydrocarbons quite rapidly when dosed with high levels. In constrast to the results observed with fish and birds, Payne and May (1979) were unable to induce AHH in lobsters chronically exposed to petroleum for as long as 6 months.

Low MFO levels have also been found in tissue preparations from a few representative species belonging to other invertebrate phyla including Echinodermata and Annelida (Payne and May 1979; Lee and Singer 1980). The pattern of metabolites produced from such model substrates as B[a]P have also not been investigated in these species. Many invertebrate species appear not to have been examined for MFO activity; these include members of such phyla as Platyhelminthes, Rhychocoela, Rotifera, Gastrotricha, Nematoda, Echiurida, Brachiopoda, Phoronida and Chaetognatha (Lee 1981). It is of interest that a recent report by Zahn et al. (1982) failed to demonstrate AHH activity in at least one species of sponge (Phylum Porifera).

3.4.2.3 Microbial Degradation

There is evidence that some aquatic microorganisms - bacteria, fungi and algae - have the enzymic capability for degrading PAHs. Although environmental water and sediment samples are composed of mixed populations, it has been found that single populations of Pseudomonas (Barnsley 1975; Dean-Raymond and Bartha 1975) and Flavobacterium (McKenna and Heath 1976), for example, can degrade PAHs. In addition, Atlas (1977) has reviewed the most frequently isolated bacterial and fungal species that degrade petroleum hydrocarbons. Bacterial genera include Pseudomonas, Acinetobacter, Flavobacterium, Brevibacterium, Corynebacterium, Arthrobacter and Mycobacterium; fungal genera include Cladosporium, Candida, Rhodotorula, Trichosporium and Torulopsis.

Some of the earliest work on microbial degradation (Sisler and Zobell 1947) describes the complete oxidation, to CO_2, of 6 PAHs ranging in size from naphthalene to dibenzanthracene (isomer not specified) after incubation for 4 days at 32°C with mixed cultures of

microorganisms of marine origin. The lower-molecular-weight compounds such as anthracene and phenanthrene were more extensively degraded to CO_2 (64 and 68%, respectively) than was the 5-ring PAH dibenzanthracene (13%) after four days.

Analysis of the first detectable products of PAH degradation indicates that bacteria convert PAHs to cis-dihydrodiols via the dioxygenase enzymatic system (Gibson et al. 1975; Gibson 1976), whereby both atoms of molecular oxygen are incorporated into the metabolite. The production of a cis-dihydrodiol appears to be the necessary step prior to enzymatic cleavage. In animals, PAHs are metabolized through the cytochrome P-450 (monooxygenase) enzymatic system to produce trans-dihydrodiols from reactive arene oxide intermediates. There is also evidence that the terrestrial fungus, Cunninghamella elegans, metabolizes naphthalene, B[a]P and 7-methylbenz[a]anthracene, to their trans-dihydrodiols; an enzyme system similar to mammalian monooxygenases has been implicated (Cerniglia and Gibson 1978; Cerniglia et al. 1982).

Co-metabolic phenomena (in which one hydrocarbon acts as a substrate for growth and a second, which cannot act as a growth substrate, is degraded by the same process) have been observed (Chou and Bohonos 1979). A number of nitrogen and sulfur-containing HACs were resistant to degradation by mixed microbial cultures from environmental water samples when added as the sole carbon source. The addition of naphthalene or anthracene as a co-substrate resulted in the degradation of benzo[b]thiophene and dibenzothiophene; quinoline added to cultures containing benzo[f]quinoline increased its degradation rate. Similarly, McKenna and Heath (1976) isolated species of Flavobacterium that degraded B[a]P, benz[a]anthracene and dibenz[a,h]anthracene in the presence of a nutrient source, phenanthrene.

The degradation rates of PAHs may be affected by many factors such as redox state, temperature, nutrient content, sediment structure and bioavailability (Gardner et al. 1979; Brink 1981). Rate constants derived under laboratory conditions cannot exactly duplicate all the variables from environmental situations. Therefore, only a few of the published rate constants are suitable for extrapolation to environmental conditions.

Roubal and Atlas (1978) and Fedorak and Westlake (1981) have described marine bacterial populations that will degrade PAHs at temperatures of 5 and 8°C, respectively. In both studies, nitrogen and phosphorus nutrient supplementation increased the degradation rates. Roubal and Atlas showed, however, that microbial degradation could occur without nutrient supplementation under natural conditions in water samples from the Beaufort Sea.

Delaune et al. (1981) have studied the degradation of B[a]P in estuarine sediment under controlled pH and redox potentials. The optimum condition for the degradation of B[a]P was under aerobic

conditions (+500 mV) with sediment pH 8.0. Gardner et al. (1979) noted a differential of an order of magnitude in PAH degradation rates between surface and subsurface crude-oil-treated sediments. This difference was less pronounced in samples from sediment containing the benthic polychaete worm Capitella capitata. Activity of the worms could contribute to aeration of sediments and mixing of nutrients within sediments, resulting in more extensive microbial growth and consequent hydrocarbon degradation.

Degradation rates for various PAHs have been related to their structure under a variety of conditions with mixed microbial populations from sediment and water (Walker et al. 1975; Herbes and Schwall 1978; Lee et al. 1978; Roubal and Atlas 1978; Fedorak and Westlake 1981; Herbes 1981; Readman et al. 1982). The overall pattern was that naphthalene was the most quickly degraded, with turnover times getting progressively longer with increasing molecular weight. Lee et al. (1978) measured the rate of microbial degradation in water from control and oil-contaminated enclosures and found that methylnaphthalene and naphthalene were more quickly degraded than benz[a]anthracene, B[a]P or anthracene. Readman et al. (1982) described degradation rates of 72 and 0.035% for naphthalene and B[a]P, respectively, in estuarine waters and they predicted that while microbial degradation could be the principal fate of naphthalene in the estuary, high microbial refractivity and particle affinity of B[a]P would lead to its accumulation in bottom sediments.

Comparison of rate constants for microbial degradation of PAH compounds in water and sediment samples from the same stream, using an upstream unpolluted site as a control, were tabulated by Herbes (1981) (Table 3-39). Degradation rate constants in sediments were highest for low-molecular-weight PAHs and decreased with increasing complexity of the PAH molecule. Lack of degradation of the larger 5-ring PAHs (benzo[a]pyrene, dibenz[a,h]anthracene) may be due in part to these compounds being so strongly sorbed to sediments that their availability to microorganisms in interstitial water is extremely low (see Section 3.4.2.1).

Herbes and Schwall (1978) have calculated rate constants for the degradation of several PAHs by mixed bacterial cultures from oil-contaminated and pristine stream sediments (Table 3-40). These data indicate that degradation proceeds at a much faster rate in sediments from the oil-contaminated stream. A greater biodegradative capacity of microbial populations from sites with a history of contamination has been indicated by a number of authors (Sherill and Sayler 1980; Chou and Bohonos 1979; Readman et al. 1982). This could be due either to a higher microbial biomass or to a microbial population enriched with hydrocarbon degraders.

Table 3-39. Degradation rate constants (k) and half-lives ($t_{\frac{1}{2}}$) for mixed bacterial populations in water and sediment from the same stream (from Herbes 1981).

	Sediment		Water	
	$k(h^{-1})$	$t_{\frac{1}{2}}$	$k(h^{-1})$	$t_{\frac{1}{2}}$
Naphthalene	7.6×10^{-2}	9 h	3.2×10^{-3}	9 d
Anthracene	1.6×10^{-2}	43 h	2.0×10^{-3}	15 d
Benz[a]anthracene	3.3×10^{-3}	208 h	nd[α]	
Benzo[a]pyrene	3.4×10^{-4}	83 h	nd	
Dibenz[a,h]anthracene	1.2×10^{-4}[β]	166 h	nd	
Dimethylbenz[a]anthracene	-	-	nd	

[α] nd = not detectable.

[β] One determination.

Table 3-40. Degradation rate constants (k) and half-lives ($t_{\frac{1}{2}}$) for mixed bacterial populations in oil-contaminated and pristine stream sediments (from Herbes and Schwall 1978).

	Oil-contaminated stream sediments		Pristine stream sediments	
	$k(h^{-1})$	$t_{\frac{1}{2}}$	$k(h^{-1})$	$t_{\frac{1}{2}}$
Naphthalene	.14	5 h	$<4 \times 10^{-4}$	>72 d
Anthracene	2.5×10^{-3}	12 d	2.5×10^{-4}	115 d
Benz[a]anthracene	1.0×10^{-4}	288 d	4.0×10^{-6}	20 a
Benzo[a]pyrene	$<3 \times 10^{-5}$	>2½ a	$<3.0 \times 10^{-5}$	>2½ a

4.0 EFFECTS ON AQUATIC BIOTA

4.1 TOXICOLOGY

4.1.1 ACUTE TOXICITY

A number of acute toxicity studies have been conducted on aquatic species with specific compounds such as naphthalene, which constitute a major fraction of the aromatic component in crude oils (Anderson et al. 1974a, b; Caldwell et al. 1977). Fewer investigations have been carried out with higher-molecular-weight compounds (> 3 rings). The LC_{50} values for PAHs in a number of species are presented in Table 4-1. Naphthalene and a number of its methylated derivatives are acutely toxic to several marine invertebrates in the range 1-5 $mg.L^{-1}$, with toxicity increasing with the degree of alkylation of the aromatic nucleus (Ott et al. 1978). A few compounds in the fluorene and phenanthrene series have been shown to be similar in toxicity to naphthalene. Studies with petroleum (which will not be discussed in detail) also indicate that naphthalene and phenols, and not the larger numbered-ring PAHs, are mainly responsible for acute toxicity (Anderson et al. 1974a; Rossi et al. 1976).

Circumstantial evidence for the lack of acute toxicity of higher-molecular-weight PAHs comes from trials in which various aquatic species were exposed to relatively high concentrations of the compounds in order to induce MFO activity. Several investigators (e.g. Philpot et al. 1977; Bend et al. 1979; James and Bend 1980) report having injected a variety of marine species with 10 $mg.kg^{-1}$ of dibenz[a,c]anthracene or 21 $mg.kg^{-1}$ of 3-methylcholanthrene with apparently no toxic effects. Freshwater species such as rainbow trout (Salmo gairdneri) also withstood the injection of up to 30 $mg.kg^{-1}$ B[a]P (Gerhart and Carlson 1978). Water and sediment contaminated with high levels of PAHs also appeared not to be acutely toxic to a number of fish and invertebrates (Lee and Singer 1979; Payne and May 1979).

Heterocyclic aromatic compounds, including a number of aza-arene compounds, are found in significant concentrations in synthetic fuels, petroleum and combustion by-products. The acute toxicity of a few of these compounds was investigated in the zooplankter Daphnia pulex (Table 4-2) and it was observed that the toxicity of these compounds increased by approximately one order of magnitude with the addition of an aromatic ring to the structure (Southworth et al. 1978b). A 48-h LC_{50} for 6-methylquinoline in Daphnia magna was found to be within this range of toxicity (Herbes and Beauchamp 1977). Bioconcentration factors for each compound also increased with increasing size of the aromatic nucleus and the authors suggested that toxicity was probably related to bioconcentration potential.

Petroleum is rich in relatively toxic naphthalene hydrocarbons and the literature indicates that it is reasonable to assume that the acute toxicity associated with such major environmental inputs as oil spills is partially attributable to these compounds. Studies also

Table 4-1. Comparative toxicity of PAHs to aquatic animals. Values are LC_{50} concentrations expressed in $mg.L^{-1}$ (Asterisk * indicates compound was not toxic within solubility limits; - indicates no data available).

Compound	Copepod[α] (24-h)	Amphipod[β] (48-h)	Amphipod[γ] (96-h)	Polychaete[δ] (96-h)	Shrimp[ε] (96-h)	Shrimp[ζ] (96-h)	Crab larvae[η] (96-h)	Shrimp[θ] (24-h)	Minnow[ι] (24-h)
Naphthalene	3.8	5.0	2.7	3.8	2.4	2.6	>2.0	2.5	2.4
1-methylnaphthalene	-	-	-	-	-	-	1.9	-	3.4
2-methylnaphthalene	1.5	-	-	-	1.1	1.7	1.3	0.7	2.0
Dimethylnaphthalene	0.9	-	-	2.6	0.7	0.7	0.6	0.08	5.1
Trimethylnaphthalene	0.3	-	-	2.0	-	-	-	-	-
Phenanthrene	-	-	-	0.6	-	-	-	-	-
Methylphenanthrene	-	-	-	0.3	-	-	-	-	-
Fluorene	-	-	-	1.0	-	-	-	-	-
Fluoranthrene	-	-	-	0.5	-	-	-	-	-
Chrysene	-	-	-	*	-	-	-	-	-
B(a)P	-	-	-	*	-	-	-	-	-
1,2,5,6-DBA	-	-	-	*	-	-	-	-	-

α *Eurytemora affinis*, Ott *et al.* 1978.

β *Parhyale* sp., cited in Lee and Nichol 1978.

γ *Elasmopus pectenicrus*, Lee and Nichol 1978.

δ *Neanthes arenaceodentata*, Rossi and Neff 1978.

ε *Palaemonetes pugio*, Neff *et al.* 1976.

ζ *Palaemonetes pugio*, Anderson *et al.* 1974b.

η *Cancer magister*, Caldwell *et al.* 1977.

θ *Penaeus aztecus*, Anderson *et al.* 1974b.

ι *Cyprinodon variegatus*, Anderson *et al.* 1974b.

Table 4-2. Toxicity (24-h LC_{50}) and bioconcentration factors (BCF) of some azaarenes to a zooplankter, Daphnia pulex (from Southworth et al. 1978b).

Compound	LC_{50} ($\mu g.L^{-1}$)	BCF
Benz[a]acridine	0.4	350
Acridine	2.9	30
Isoquinoline	39.9	2.5

suggest that higher-molecular-weight PAHs probably play a minor role in acute toxicity. The levels of PAHs demonstrated to be toxic to aquatic animals are generally much higher than levels found in the aquatic environment, except for PAH concentrations that might be found at sites such as the immediate vicinity of oil spills.

The limited information available suggests that HACs such as azaarenes, which may become more environmentally important in Canada through the development of various synthetic fuel technologies, may have a significant acute toxicity potential. This would probably be more relevant in relation to freshwater environments.

4.1.2 SUBLETHAL TOXICITY

Various types of sublethal responses have been obtained in laboratory studies with PAHs. In assessing the importance of sublethal or stress effects of contaminants, it is important to distinguish between effects within the normal response range of the organism and those effects truly detrimental to the survival of the organism or the species. The role of stress in the survival of organisms has been developed and reviewed by Selye (1976, 1977) and necessitates relatively complex dose level/time experiments to assess adequately whether the animal is responding within its normal capacity or in a state of collapse (e.g. Freeman et al. 1982). Studies on stress are further complicated by handling and sampling effects. Bouck and Ball (1966) and Love (1970) have pointed out that these experimental procedures are often a source of major changes in blood parameters of fish. Problems associated with the use and interpretation of sublethal effect observations in organisms have been recently reviewed (cf. Uthe et al. 1980).

Bacteria

Relatively high PAH concentrations appear to affect bacterial growth. For instance, Hass and Applegate (1975) studied the effect of several PAHs on the growth of the bacterium Escherichia coli and noted that high concentrations (10^{-7} - 10^{-5} M range) generally inhibited bacterial growth. Calder and Lader (1976) also tested a number of high-molecular-weight PAHs, in addition to naphthalene and its derivatives, on two species of non-hydrocarbon degrading marine bacteria. Under laboratory conditions, phenanthrene and B[a]P decreased the growth rate of Serratia marinorubra and Vibrio parahaemolyticus, as did naphthalene and its derivatives. Conversely, pyrene was found to stimulate bacterial growth. The magnitude of inhibition (toxic effect) was found to be a function of two parameters, exposure concentration and inherent toxicity. Thus B[a]P, with a greater toxicity at a concentration of 0.02 µM (5 $\mu g.L^{-1}$), exerted a toxic effect similar to naphthalene at 100 µM (12.8 $mg.L^{-1}$).

Plants

Several PAHs at concentrations in the range 10-20 $\mu g.L^{-1}$ stimulated growth in various species of freshwater algae (Graf and Nowak 1966) and similar results were reported by Boney and Corner (1962) in studies on sprouting growth in the marine red alga Antihamnion. However, it has also been observed that relatively high concentrations of PAHs ($\approx$ 0.3 $mg.L^{-1}$) inhibited the growth of A. plumaria sporelings. Bastian and Toetz (1982) noted variable effects of PAHs on the biomass of the blue-green alga Anabaena flos-aquae. At all concentrations in the range of 10-96% of saturation (up to 14 $mg.L^{-1}$), naphthalene stimulated growth, pyrene had no effect, and phenanthrene, fluorene, chrysene and benzanthracene inhibited growth.

Cell division was inhibited in Chlorella vulgaris exposed to naphthalene at concentrations of 3-30 $mg.L^{-1}$, but the algae appeared to recover rapidly after one or two days exposure (Kauss and Hutchinson 1975). Similar high concentrations of naphthalene inhibited photosynthesis in Chlamydomonas (Kauss et al. 1973). Vandermeulen and Ahern (1976) also noted inhibition of photosynthesis in unicellular marine algae exposed to 1 $mg.L^{-1}$ naphthalene, but cells resuspended in naphthalene-free medium regained normal photosynthetic rates after a few hours. A concentration of 10 $\mu g.g^{-1}$ naphthalene inhibited photosynthesis, as evidenced by $^{14}CO_2$ assimilation, by as much as 50% in a naturally-occurring mixture of freshwater phytoplankton and as much as 37% in marine phytoplankton (Kusk 1981). Phenanthracene, at a concentration of 1.0 $\mu g.g^{-1}$, decreased photosynthetic activity by as much as 50% and 14% respectively in the two populations. At nearly all concentrations of naphthalene and phenanthrene, inhibitory effects were greater in marine algae populations. Aromatic compounds from coal conversion effluents were found to cause short-term photosynthetic inhibition in the alga Selenastrum capricornutum (Giddings 1979). The concentrations used were expressed as % of a saturated solution for most compounds tested, so that it is difficult to compare toxicity on a weight-to-volume basis without solubility factors. Among those compounds tested were quinones, amines, phenols, PAHs, thiophenes and azaarenes, all of which were found to affect algal photosynthesis. It is important to note that the short-term effects on growth and photosynthesis recorded in laboratory studies with unicellular algae support observations made at oil spill sites where transient effects on primary productivity have also been recorded (Smith 1968; Straughan 1971).

Echinoderms

There have been a few reports on the effects of PAHs on embryonic development in sea-urchins. Bresch et al. (1972) reported that the development of the sea urchin Psammechinus miliaris was unaffected by exposure to 1-2 $\mu g.mL^{-1}$ of B[a]P (administered as an

albumin adduct) if exposure was initiated after fertilization. Similar observations were made by Ceas (1974) in newly fertilized eggs of sea-urchins (Paracentrotus lividus) exposed to 5 $\mu g.mL^{-1}$ serum B[a]P. Effects have been noted in embryonic development during chronic exposure. For instance, abnormalities were observed in the embryos of P. lividus exposed to the carcinogen 7,12-dimethylbenzanthracene at 10^{-5} M.

Molluscs

A number of studies have focused on the sublethal effects of PAHs or PAH-containing mixtures such as petroleum. A variety of responses such as changes in cell lipids, number of lysosomal granules and shell growth rates have been observed in molluscs chronically exposed to relatively low concentrations of petroleum in the field as well as in the laboratory (e.g. Gilfillan and Vandermeulen 1978; Wolfe et al. 1981). These will not be reviewed in detail but it is reasonable to assume that PAHs, especially low-molecular-weight PAHs, may be partially responsible for some of the observed effects. For instance, it is especially interesting to note that the reduced tissue and cell growth observed in bivalves (Gilfillan and Vandermeulen 1978), at the site of the Arrow tanker spill in Nova Scotia, were due to a No. 6 (bunker) oil, which was deficient in monoaromatic compounds but highly enriched in PAHs (see Section 3.2.2.2.1).

In reference to trials with PAHs in the laboratory, the heart rate of mussels (Mytilus californianus) was depressed in animals exposed to very high levels of B[a]P (10 $mg.L^{-1}$) (Sabourin and Tullis 1981). Preliminary studies on a number of immunological parameters in the hardshell clam, Mercenaria mercenaria (Anderson 1981) have indicated that long exposure (18 wk) and low dose (not indicated) exposures to B[a]P impaired the overall ability of the mollusc to eliminate a standard dose of injected bacteria. Of greater relevance, Moore et al. (1978) noted the dose-dependent destabilization of lysosomal membranes in the digestive cells of mussels injected with several representative PAHs. Short exposure periods to low levels of petroleum hydrocarbons in seawater have also been shown to destabilize liposomal membranes (Widdows et al. 1982). Other responses that were significantly altered by short(4 wk)- or long(5 mo)-term exposures were rates of oxygen consumption, feeding, excretion and scope for growth, digestive cell size, and specific activities of several enzymes. These results are of particular interest since the responses were obtained with environmentally realistic exposures to hydrocarbons.

Crustaceans

Most laboratory observations on the sublethal effects of PAHs have been carried out with various species of crustaceans. Ott et al.

(1978) studied the sublethal effects of naphthalene and its methylated derivatives on an estuarine copepod Eurytemora affinis and observed that levels of approximately 10 $\mu g.L^{-1}$ caused a significant reduction in lifespan as well as in the reproductive capacity of females. The effect of PAHs on sinking rates was investigated in barnacle nauplii (Balanus amphitrite niveus) (Donahue et al. 1977) (Table 4-3). Diaromatic compounds were more toxic than triaromatic compounds with the exception of anthracene, which did not display toxicity. The negative response reported for anthracene is probably related to its relatively low aqueous solubility.

Variability in environmental factors may be important in modulating PAH toxicity. Laughlin and Neff (1979, 1980) examined the interactive effects of salinity, temperature and exposure to either phenanthrene or naphthalene on the development rates of mud crab larvae (Rhithropanopeus harrisii). The toxicity of naphthalene was much less than that of phenanthrene, particularly at high temperature (30°C) and low salinity (5 $^{0}/_{00}$). Temperature was a marginally significant physical factor but low salinity was a prominent factor in reducing animal tolerance to phenanthrene. This is an important consideration in estuarine organisms, since any factor reducing tolerance in low salinity conditions could be detrimental to population survival.

Some crustacean studies have demonstrated relative insensitivity to toxic low-molecular-weight PAHs. For instance, the survival of Dungeness crab (Cancer magister) was not affected by chronic exposure to naphthalene at a concentration of 10-170 $\mu g.L^{-1}$ (Caldwell et al. 1977) and exposure of grass shrimp (Palaemonetes pugio) to phenanthrene concentrations of 25-100 $\mu g.L^{-1}$ had no effect on larval survival (Young 1977). Growth was reduced in grass-shrimp larvae exposed to phenanthrene, but the animals recovered upon return to clean water. Such transient growth inhibition is probably due to such effects as decreased feeding rates and/or general increase in respiration rates.

Fish

A few studies have investigated the chronic effects of petroleum on fish. Payne et al. (1978a) noted changes in testes size, eye-lens diameter, and serum chloride but found no evidence for tissue histopathology in fish exposed to ≈ 1 $mg.L^{-1}$ petroleum for 5 months. Liver hypertrophy, characterized by increased lipid content, was observed in winter flounder (Pseudopleuronectes sapidus) exposed to petroleum-contaminated sediment (Fletcher et al. 1982). The concentration of petroleum used in this experiment with flounder was quite high (2000-4000 $\mu g.g^{-1}$) but similar concentrations can be expected in intertidal/nearshore sediments heavily impacted with petroleum. However, it is of interest that in animals exposed to as much as 2000 $\mu g.g^{-1}$ weathered oil in sediment, the observed effects were diminished. Weathered oil is enriched in high-molecular-weight compounds, including

Table 4-3. Effect of some PAHs on barnacle nauplii (Balanus amphitrite niveus) (from Donahue et al. 1977).

Compound	Value of the 1-h ED_{50}[α]	
	% saturated solution in seawater (30 °/oo)	µg.g^{-1} seawater[β]
Naphthalene	13	2.6
Dimethylnaphthalene	6	.14
Fluorene	44	.35
Phenanthrene	70	.42
Anthracene	no effect	-

[α] Concentration of PAH at which half the larvae sank to the bottom after 1-h exposure.

[β] Saturation concentration data for seawater (32 °/oo at 22°C) for conversion to µg.g^{-1} seawater from Rossi and Neff (1978).

PAHs, and deficient in toxic monoaromatic compounds (e.g. Boehm et al. 1981), suggesting that relatively high PAH levels in sediment may be required before adverse effects are produced in ground fish. Attempts to induce reproductive effects in trout by feeding very high concentrations (0.1%) of crude oil in food for prolonged periods were unsuccessful (Hodgins et al. 1977a). Ingestion of B[a]P five hours before spawning has been found to affect the reproductive success of flathead sole (Hippoglossoides elassodon) (Hose et al. 1981). A significantly lower hatching success was noted in eggs from female fish fed B[a]P (11.9%) than in control eggs (56.6%) and the incidence of embryonic abnormalities rose from 1.6% to 5.6%. Growth or behavioral differences were not noted between larvae from the two groups. This result is also of special interest since sublethal effects on fish reproduction are of particular ecological relevance.

Aquatic Birds

Water birds may be exposed to PAHs that occur as components of crude and refined oils in surface spills. Oil on the plumage, feet or nesting material may be ingested during preening or transferred to eggs during incubation. Although most research on sublethal effects deals with the effects of crude oil and fuel oil, several studies have indicated that toxicity of oils resides in the aromatic fraction (Albers 1977; Hoffman 1979; Hoffman and Gay 1981; Peakall et al. 1982; Ellenton 1982). Albers (1977) found that the application of µL-quantities of fuel oil to the egg surface was embryotoxic to mallards (Anas platyrhynchos). The application of a mixture of aliphatic hydrocarbons had only a small effect and the author concluded that the embryotoxic effects of crude oil were due to substances other than aliphatic hydrocarbons. Experiments by Hoffmann (1979) indicated that when 20 µL of a mixture of aromatic hydrocarbons, representative of that in crude oil, was applied to the surface of mallard eggs on day 3 of incubation, the viable embryos decreased from 98% (untreated and aliphatic hydrocarbon treated controls) to 42%. The percentage of abnormal survivors increased from 4 to 18. Application of individual aromatic hydrocarbon components alone or in combination had either a small or no effect. Addition of the PAHs chrysene, B[a]P and 7,12-dimethylbenz[a]anthracene (DMBA) to the aromatic mixture greatly enhanced its embryotoxic and teratogenic effects in the order DMBA > B[a]P > chrysene (Hoffmann and Gay 1981).

Prudhoe Bay crude oil, or its high-molecular-weight aromatic fraction, depressed the growth rate and increased the nasal and adrenal gland weight when 1 mL was administered to nestling herring gulls (Larus argentatus) (Peakall et al. 1982). In comparison, the lower-molecular-weight aromatic fraction, composed mainly of 2- and 3-ring PAHs, had no significant effect on those parameters measured.

4.1.3 MUTAGENESIS-CARCINOGENESIS

Concern about PAHs stems primarily from their carcinogenic potential. The relative carcinogenicity of some PAHs and azaarenes is summarized in Table 4-4 (USNAS 1972). The general relationship of structure to carcinogenic activity seems to favor the 4-, 5-, and 6-ring PAHs rather than smaller (anthracene, phenanthrene) or larger (coronene) molecular weight compounds.

Carcinogenesis is usually emphasized in discussions on PAHs, but it is also important to note that mutagenesis and teratogenesis are important aspects; the mechanisms of toxicity for all three could be similar at the cellular level. It is believed that PAHs require metabolic activation to exert their carcinogenic (and putative mutagenic and teratogenic) effects, with carcinogenesis being initiated by the binding of reactive electrophilic metabolites to critical cellular constituents (Wislocki et al. 1976). The photodynamic activity of PAHs has also been suggested as a possible mechanism for their activation (Morgan and Warshawsky 1977). In an attempt to define the mechanisms of action, structure-activity relationships have been proposed with the most current being the bay-region theory. The "bay region" of an aromatic hydrocarbon is typified by the hindered, angular region between the 4 and 5 positions in the phenanthrene molecule (see Appendix I). When epoxides form part of the bay region, they have been found to be extremely reactive (Jerina et al. 1977) and diol-epoxides in the bay region possess even higher mutagenic activity (Wislocki et al. 1976). Benzylic carbonium ions are more easily formed in these compounds and Jerina et al. (1977) suggest that this property may be a good index of biological reactivity. The reader is referred to recent reviews (e.g. Gelboin 1980; Zedeck 1980) for more discussion in this area.

Studies on mammalian systems have demonstrated a role for mixed-function oxygenases (MFO) in the activation of aromatic hydrocarbons to specific mutagenic, carcinogenic and cytotoxic metabolites. Recent studies with fish have also shown that B[a]P metabolites can covalently bind to cell macromolecules, both in vitro (Ahokas et al. 1976; Varanasi and Gmur 1980) and in vivo (Varanasi et al. 1981). It is known from mammalian systems that many PAHs do not yield carcinogenic-mutagenic metabolites, and only certain metabolites of known carcinogens are active. Also, biochemical investigations to date on reactive metabolite formation in fish have been limited to binding studies with single compounds - namely the potent mutagen-carcinogen, benzo[a]pyrene. Laboratory studies of the chronic effects of PAHs on mussels have not been performed, but Neff (1979) suggests they would provide interesting information on PAH-induced carcinogenesis in light of the facts that: 1) the majority of bivalve molluscs have so far been found to have very low MFO activity and so should be unable to metabolically activate PAHs; and 2) there have been reports of bivalve populations with high incidences of neoplasms, some of these from oil-polluted areas (see Section 4.2.4).

Table 4-4. Relative carcinogenicity of some PAHs and azaarenes tested in mammals (- indicates compound not carcinogenic; ±, uncertain or weakly carcinogenic; +, carcinogenic; ++, +++, ++++, strongly carcinogenic) (from USNAS 1972).

Compound	No. of rings	Carcinogenicity index
Anthracene	3	-
Benz[a]anthracene	4	+
7,12-dimethylbenz[a]anthracene	4	++++
Dibenz[a,j]anthracene	5	+
Dibenz[a,h]anthracene	5	+++
Dibenz[a,c]anthracene	5	+
Phenanthrene	3	-
Benzo[c]phenanthrene	4	+++
Fluorene	3	-
Benzo[a]fluorene	4	-
Benzo[b]fluorene	4	-
Benzo[c]fluorene	4	-
Dibenzo[a,g]fluorene	5	+
Dibenzo[a,h]fluorene	5	±
Dibenzo[a,c]fluorene	5	+
Fluoranthene	4	-
Benzo[b]fluoranthene	5	++
Benzo[j]fluoranthene	5	++
Benzo[k]fluoranthene	5	-
Benzo[m,n,o]fluoranthene	5	-
Aceanthrylene	3	-
Benz[j]aceanthrylene (cholanthrene)	4	++
3-methylcholanthrene	4	++++
Naphthalene	4	-

Table 4-4. (Cont'd)

Compound	No. of rings	Carcinogenicity index
Pyrene	4	-
Benzo[a]pyrene	5	+++
Benzo[e]pyrene	5	-
Dibenzo[a,l]pyrene	6	±
Dibenzo[a,h]pyrene	6	+++
Dibenzo[a,i]pyrene	6	+++
Dibenzo[cd,jk]pyrene	6	-
Indeno[1,2,3-cd]pyrene	5	+
Chrysene	4	±
Dibenzo[b,def]chrysene	6	++
Dibenzo[def,p]chrysene	6	+
Dibenzo[def,mno]chrysene (ananthrene)	6	-
Perylene	5	-
Benzo[ghi]perylene	6	-
Coronene	7	-
Acridine	3	-
Dibenz[a,j]acridine	5	++
Dibenz[a,h]acridine	5	++
Dibenz[c,h]acridine	5	±
Carbazole	3	-
Benzo[a]carbazole	4	±
Dibenzo[a,g]carbazole	5	±
Dibenzo[c,g]carbazole	5	+++
Dibenzo[a,j]carbazole	5	±

Of more importance in the environment is the fact that PAHs are present as complexes and therefore, the biological responses to individual PAHs may be modified by non-carcinogenic PAHs. For instance, non-carcinogenic PAHs taken up by organisms can be expected to modify the formation of reactive metabolites at the MFO level.

Enzyme systems other than MFO, which may influence the rate of production or degradation of reactive PAH metabolites (e.g. epoxide hydratases, glutathione-S-transferases), are found in aquatic animals (James et al. 1979b) and can also be expected to play an important role in toxicity. It is presently not known if the levels of these enzymes are dependent upon intrinsic and extrinsic factors.

Short-term mutagenicity tests are valuable for screening carcinogens that form reactive electrophiles; in fact, a major theory of carcinogenesis suggests that cell mutagenesis is a necessary step for the initiation of cell transformation (Wilson 1981). Several studies with marine and freshwater fish species have demonstrated the capacity of fish liver enzymes to bioactivate PAHs into mutagens, as demonstrated in short-term assays (Ahokas et al. 1976; Payne et al. 1978b; Kurelec et al. 1979; Melius et al. 1980) (Table 4-5). Lindmark (1981) has observed activation of 2-aminofluorene by a marine ciliate, but the activation of such amino-substituted PAHs may not be mediated by MFO. Neither fish extrahepatic tissues nor various invertebrate tissues appear to have been investigated in short-term mutagenic assays with such model PAH mutagens as B[a]P.

Concern has been expressed that petroleum sources of PAHs may be important in marine environmental carcinogenesis (e.g. Zobell 1971). Payne et al. (1979) tested PAH-enriched fractions of a large number of different types of petroleum in the Ames Salmonella typhimurium assay but none was found to be mutagenic (effective in causing at least a doubling in numbers of revertant colonies when applied in various sub-toxic concentrations). Similar results have been reported by other groups in mutagenic assays with crude oils (Pelroy et al. 1981), tar sands (Shahin and Fournier 1978) and coal extracts (Stahl et al. 1983). Nevertheless, mutagenic activity has been demonstrated, though often at low levels in crude oils fractionated to various degrees (Ellenton and Hallett 1981). It is likely that when complex mixtures are assayed for mutagenic activity, traces of mutagenic PAHs such as B[a]P, which are found in petroleum, are effectively masked in the presence of large numbers of non-mutagenic compounds. Support for this idea has come from studies on combustion byproducts and B[a]P, in which activity was quite effectively inhibited in the presence of petroleum extracts (Hermann et al. 1980; Rahimtula et al. 1982). Such anti-mutagenic effects could be due to competitive inhibition by many potential substrates at the level of enzyme activation. Inhibition of PAH-mediated carcinogenesis in the presence of non-carcinogenic PAHs has also been demonstrated in cancer studies with mammals (e.g. Schmeltz et al. 1978). However, conditions can also be postulated in which non-carcinogenic PAHs may enhance

Table 4-5. Bioactivation of PAHs to mutagens by aquatic animals (as shown in the Ames Salmonella/microsome short-term mutagenicity assay).

Compound	Species	Reference
Used crankcase oil	rainbow trout (Salmo gairdneri)	Payne et al. (1978b)
Benzo[a]pyrene	lake trout (Salmo trutta lacustris)	Ahokas et al. (1976)
2-acetylaminofluorene	"	"
Benzo[a]pyrene	carp (Cyprinus sp.) mullet (Mugil cephalus)	Kurelec et al. (1979)
2-Aminofluorene	marine ciliate (Parauronema acutum)	Lindmark (1981)
2-acetylaminofluorene	"	"

carcinogenesis - for instance, through such mechanisms as MFO enzyme induction. In reference to the aquatic environment, it is important to note that PAH complexes, and not single compounds, are of most interest and compound interaction can be expected to play an important role in any potential for mutagenesis/carcinogenesis.

In contrast to results obtained in mutagenic assays with PAH-enriched fractions of petroleum, many studies have established that crude extracts of diesel engine soot, gasoline engine soot, and used engine oil are rich sources of potent mutagens (Payne et al. 1978b; Wang et al. 1978; Löfroth 1980). Some of these mutagens act directly while others appear to require MFO activation. The discovery that combustion hydrocarbons contain potent mutagens is of particular interest since relatively large concentrations of these compounds enter the aquatic environment via urban runoff or atmospheric deposition (see Section 3.3). Much of the mutagenic activity associated with combustion byproducts is believed to be due to nitro-substituted PAHs and some of these compounds (e.g. 1-nitropyrene) have recently been shown to be very potent mutagens (cf. Rosenkranz et al. 1980; Campbell et al. 1981). The new synthetic fuel technologies have also been found to be a source of mutagenic PAHs (Guerin et al. 1980; Wilson et al. 1980), many of which may be nitro- or amino-substituted compounds. Many nitro- substituted compounds do not require activation by the cytochrome P_{450} enzyme system but can also be activated by various "types" of reductase enzymes. Indeed, the fact that these compounds are found to be direct-acting in the Salmonella typhimurium assay is indicated to be due to the presence of activating reductase enzymes in the bacterial strains (e.g. Rosenkranz et al. 1980). Thus, even those animals having relatively low levels of MFO enzymes, such as many species of invertebrates, may be quite effective in activating many nitro-substituted PAH compounds. For instance, in a study by Elmamlouck and Gessner (1976), nitroreductase activity was readily detectable in lobster hepatopancreas whereas MFO catalytic activities were not.

Although evidence indicates that various combustion processes may provide the aquatic environment with rich sources of mutagenic PAHs, it is premature to suggest that such compounds are invariably involved in aquatic mutagenesis/carcinogenesis. For instance, diesel exhaust extracts contain potent mutagens although whole diesel exhaust does not appear to be mutagenic in mammalian systems (USNRC 1981). Also, laboratory animals appear to be quite refractory to the chronic exposure (by inhalation) to diesel or gasoline enzyme exhaust (USNRC 1981). Bioavailability is believed to play a critical role in carcinogenesis experiments in which potential cancer-producing compounds are associated with particulates. It is important to note that in the aquatic environment there would also be another level of bioavailability, namely bioavailability from water or sediments, which could be a major limiting factor in PAH toxicity (see Section 3.4.2.1).

With the exception of some studies on fish and amphibians, there have been relatively few laboratory studies on the carcinogenicity

of PAH in aquatic organisms. Zebra-fish (Brachydanio rerio) exposed to 0.5 mg.L^{-1} 7,12-dimethylbenz[a]anthracene developed tumor-like growths (Pliss and Khudoley 1975) and two species of viviparous fish (Poeciliopsis lucida and P. monacha) developed liver neoplasms after repeated short-term exposures to an aqueous suspension (5 mg.L^{-1}) of 7,12-dimethylbenz[a]anthracene (DMBA) (Shultz and Shultz 1982). Three-spined stickleback (Gasterosteus aculeatus) and bitterling (Rhodeus amarus), whose skin was painted with either 3-methylcholanthrene or B[a]P twice a week for 3-6 months, developed epitheliomas (Ermer 1970). Neoplastic infiltration was observed in the underlying tissues of regenerating newt tails injected with PAHs (Neukomm 1974). The newt epidermis reacted to injected PAHs in the following order of sensitivity: dibenz[a,h]anthracene (10^{-11}-10^{-10} mg.mL^{-1}); 3-methylcholanthrene (10^{-9}-10^{-8} mg.mL^{-1}); benzo[a]pyrene (10^{-4}-10^{-3} mg.mL^{-1}); and 9,10-dimethylbenz[a]anthracene (0.1-1.0 mg.mL^{-1}). Nodule formation was observed after 9-13 days when pure crystals of 20-methylcholanthrene, B[a]P and 7,12-dimethylbenz[a]anthracene were implanted under the tail skin of larval toads (Bufo arenarium) (Matos and deLustig 1973). Formation of nodules or of accessory body structures was not observed in fluorene- or paraffin-implanted controls. Crystals of methylcholanthrene implanted into the abdomen or forelimbs of the African clawed frog, Xenopus laevis, also resulted in the production of lymphosarcoma (Ruben and Balls 1964).

Tumors developed in planarians (Phylum Platyhelminthes) exposed to either B[a]P or 3-methyl-cholanthrene in their medium (Foster 1969). Seven percent of the B[a]P-treated and nine percent of the cholanthrene-treated planaria developed tumors, which histology showed to be the result of disorganized tissue elements rather than neoplastic cells. Thirteen malformations and 12 papilliform tumors were observed in 40 offspring from the cholanthrene-treated group while the B[a]P-treated group had fewer malformations.

Various carcinogenic PAHs have been shown to produce cancer-like growths in a few aquatic species; however, experiments to date have been carried out with high concentrations of chemicals. Studies with much lower concentrations are required before deductions can be made about the relevance of such single-compound exposures to carcinogenesis in aquatic organisms.

4.2 ENVIRONMENTAL EFFECTS

4.2.1 GENERAL ECOLOGICAL EFFECTS

Adverse environmental effects have been well established in investigations on intertidal and near-shore sediments impacted with high concentrations of petroleum (a potentially rich source of PAHs) (e.g. Chan 1977; Clark et al. 1978, Cross et al. 1978). Most studies have dealt with effects on invertebrates in intertidal areas, although plaice

(Pleuronectes platessa) collected in the vicinity of the large Amoco Cadiz tanker spill displayed a variety of histopathological lesions (Haensly et al. 1982). The elevated levels of PAHs and congeners found in heavily contaminated sediments may play a role in toxicity. However, the effects of such impacts appear to be localized. A variety of studies carried out in relation to oil pollution have not been able to substantiate suggestions that trace levels of PAHs (and other toxic hydrocarbons) entering the environment have had significant ecological impacts (e.g. The Royal Society 1980; Kornberg 1982). Furthermore, information has been presented from localized studies in a major oil port (Baker 1976), offshore petroleum development sites, (e.g. Mertens 1976) as well as from studies on natural oil seeps (Straughan 1977; Davis and Spies 1981). There is also a large amount of circumstantial evidence indicating that animal populations in the vicinity of major oil spills (in non-intertidal zones) have not been irreparably harmed (reviewed by Payne 1980). In relation to information on general levels of PAHs found in biota, several studies have described PAH tissue concentrations in the $\mu g.g^{-1}$ range in animals taken from coastal and continental waters, although the presence of such tissue concentrations has not been associated with adverse animal health (DiSalvo et al. 1975; Grahl-Nielsen et al. 1978; Vanderkooy 1978; Mackie et al. 1980; Knutzen and Sortland 1982).

Most of the information available comes from studies on oil spills but it must be emphasized that any sediments containing high levels of PAHs have potential for adverse impact. For instance, the concentration of PAHs sampled from Lake Erie sediments near a large coal-oil fired power plant have been attributed with affecting the population size of polychaete worms in the area (Eadie et al. 1982). At several of the sites, concentrations of phenanthrene and fluoranthene in the sediment reached and exceeded the 96-h LC_{50} levels reported for a marine polychaete (Neff 1979; see Table 4-1). At two locations in Canada, marine sediments adjacent to a coal-coking plant in Sydney, Nova Scotia (EPS 1982) and an aluminum smelting plant in Kitimat, British Columbia (Cretney et al. 1980; Brown et al. 1983) contained up to 2830 $\mu g.g^{-1}$ (dry weight) and greater than 8 $\mu g.g^{-1}$ (wet weight) PAHs respectively. Invertebrate populations living in the vicinity had correspondingly high tissue levels of PAHs (4.12 $\mu g.g^{-1}$ and 0.04 $\mu g.g^{-1}$ wet weight). The connection between such high tissue levels of PAHs and poor health in biota has not been studied in the Nova Scotia situation; in Kitimat, their contribution to an infiltrative hyalinocytic condition in the mussel Mytilus edulis has been postulated, but not proven.

4.2.2 ADAPTIVE RESPONSE TO ENVIRONMENTAL PAHs BY MICROBES

A large amount of experimental evidence indicates that hydrocarbon-utilizing bacteria can respond to the presence of high concentrations of aromatic hydrocarbons in aquatic environments under favorable growth conditions. Field studies have also demonstrated that

oil-polluted sites support relatively large bacterial populations containing a high proportion of hydrocarbon-degrading microbes. Enrichment in hydrocarbon-utilizing populations has been documented in particular at actively worked oil-field sites in the North Sea as well as in the Gulf of Mexico (Oppenheimer et al. 1977; Holloway 1980). Field studies in the Canadian Arctic and on the East Coast also indicate low population levels of hydrocarbon-degrading bacteria (Bunch and Horland 1976; Bunch 1979), presumably reflecting the pristine nature of the environment.

4.2.3 ADAPTIVE RESPONSES TO ENVIRONMENTAL PAHs BY AQUATIC ORGANISMS

Laboratory studies by Payne and Penrose (1975) demonstrated that potentially rich sources of PAHs such as petroleum were quite effective in inducing mixed-function oxygenase activity in fish and that species collected at Newfoundland field sites with a history of hydrocarbon contamination had elevated MFO activity levels (Payne and Penrose 1975; Payne 1976). Similar elevated enzyme levels were found in other fish species collected near oil spill sites in the Atlantic and the Mediterranean (Stegeman 1978; Kurelec et al. 1977). More recently, Spies et al. (1982) reported MFO induction in fish collected near natural oil seeps off the California coast, and monitoring studies at offshore development sites in the North Sea have documented elevated enzyme levels in fish taken near some oil rigs (Davies et al. 1981). Such adaptive responses by MFO to environmental levels of PAHs are of interest in relation to general detoxification/toxicity processes in fish as well as to usage of the enzyme system in biological monitoring studies.

Persistent environmental chemicals such as PCBs, PBBs and dioxins have also been used in laboratory studies to induce MFO in fish (reviewed in Stegeman 1981). It is presently not known if threshold inducing levels of such chemicals (or similar ones) are present in the aquatic environment (e.g. bioavailability could be a major limiting factor) but it has been suggested that the level of PCBs found in some fish species in the Mediterranean may represent threshold inducing levels. In Canada, the same suggestion may be made for some species of fish in the Great Lakes that contain elevated levels of PCBs (e.g. Sonstegard and Leatherland 1979) and possibly other potent inducers.

Studies in mammalian systems have demonstrated that it is the exception rather than the rule to find even moderately lipophilic compounds which cannot act as inducers at some concentration (e.g. de Bruin 1976). Thus, many surface waters containing either "trace" levels of potent inducers such as PAHs, PCBs etc. or possibly "elevated" levels of natural inducers (such as certain sewage compounds) may have the potential to induce MFO enzymes. In contrast to fish, the situation concerning the potential for MFO induction in invertebrates is less clear. Earlier laboratory studies failed to find evidence for induction

(e.g. Payne and May 1979; Singer et al. 1980; Vandermeulen and Penrose 1978), but it has now been demonstrated in some species. Slightly elevated MFO levels have been observed in planktonic copepods exposed to 3-methylcholanthrene (Walters et al. 1979), polychaete worms (Nereis virens) fed benzanthracene, and polychaete worms (Capitella capitara) exposed to oil-contaminated sediment (Lee and Singer 1980; Lee et al. 1979d). In the last case, elevation in enzyme activity occurred over a number of generations. This demonstrates the potential for environmental adaptation to elevated levels of PAHs by genetic selection for strains with high "basal" levels of MFO enzymes.

Lee et al. (1981) also recently reported the first evidence for MFO induction (or genetic selection) in field populations of aquatic invertebrates. Both polychaetes and crabs collected at old oil spill sites in the United States were found to have elevated levels of MFO enzymes, compared with levels found at control sites. More studies are required to elucidate the characteristics of MFO induction in various invertebrate phyla.

4.2.4 TUMOR FREQUENCY AND POLLUTION

It has been observed that the frequency of occurrence of a variety of fish tumors appears to bear some relationship to elevated levels of domestic and/or industrial pollution (Brown et al. 1973, 1977, 1979; Alink et al. 1979). However, Kezic et al. (1980) and Teskeredzic et al. (1980) found elevated levels of liver B[a]P monooxygenase in several species of fish from rivers of low water quality, yet this was not correlated with incidence of neoplasia. Large numbers of individual fish appeared to be diseased but pathological reports indicated these diseases were of bacterial or viral origin. Nevertheless, Frezza et al. (1981, 1982) detected mutagenic activity in extracts of mussels (Mytilus edulis) from the Venice lagoon in the presence of indicator organisms Saccharomyces cerevisiae and Schizosaccharomyces pombe. When this mutagenic activity in mussels from the lagoon was compared with that in mussels from a clean area, a dramatic increase in both gene conversion and mutation frequency was observed. Farley (1977) has suggested that environmental factors in the form of carcinogenic contaminants such as petroleum and its constituent compounds may be etiologic agents in molluscan neoplastic diseases. Hodgins et al. (1977b) recommended that further studies are needed on the action of such chemical mixtures in the aquatic environment as direct or carcinogenic agents, or in altering the susceptibility of organisms to disease agents such as tumor viruses.

Several studies have discussed the problems associated with attempts to establish the etiology of a variety of tumors found in fish from Canadian waters. In the Great Lakes system, Sonstegard (1977) has noted the increase in gonadal tumors in natural goldfish-carp hybrids (Carassius auratus, Cyprinus carpio) over a 30-year period, and

attributed it to increases in pollution during that time. Also investigated was the incidence of white-sucker skin papilloma (Catastomus commersoni), which the author found to be greatly increased in the Oakville-Burlington area of Lake Ontario. Papilloma tended to appear on the lips of these bottom-dwelling fish and Sonstegard concluded that exposure to lake sediments was an important factor in the appearance of the tumor. Sonstegard and Leatherland (1980) have recommended the monitoring of tumor frequencies in feral aquatic organisms as a measure of detecting environmental carcinogens.

Stich et al. (1977) investigated geographic variations in the prevalence of skin papillomas in various species of flatfish (Pleuronectidae), another bottom-dwelling organism. Although fish were sampled on a worldwide basis, skin papillomas were restricted to flatfish species in the northern Pacific Ocean, Bering Sea, Sea of Okhotsk and the Japan Sea. Within this global distribution, local variations in tumor prevalence were found that were usually related to anthropogenic activity. McCain et al. (1978) found increased incidence of flatfish skin papillomas in the Bering Sea but not further north in the Gulf of Alaska, although local "hot spots" did exist. In neither study were the authors able to establish the etiology of the tumors. Stich et al. (1977) also investigated the prevalence of skin papillomas in eels and lymphocystis disease in flatfish; they found a geographic basis for the distribution of these two diseases with no apparent explanation of their etiology.

In the U.S.A., the Smithsonian Institute in Washington, D.C. operates a "Registry of Tumors in Lower Animals" (cf. Harshbarger 1982) to "facilitate the study of neoplasms and related disorders in invertebrates and poikilothermic vertebrate animals by serving as a specimen depository, a diagnostic center, an information center and a collaborative study group to help understand the nature of contributed material." Specimens are received on a worldwide basis and include both wild and laboratory specimens; periodic reports are issued. A computerized library of approximately 4000 references on neoplasms and related disorders in ectothermic animals is in the final stages of preparation (Harshbarger 1982).

The International Council for the Exploration of the Sea (ICES), made up of the eighteen countries surrounding the North Atlantic (from the U.S.A. to Portugal), has recommended (ICES 1981) that "member countries should, whenever possible, undertake observations on pathobiology (e.g. tumors, fin rot, skeletal abnormalities) in relation to environment." This program is being carried out in an attempt to develop monitoring studies of the effects of marine contamination.

The "Mussel Watch" program in the U.S.A., although originally designed as a monitoring system of environmental levels of chemical contamination, has been expanded to include histological and biochemical investigations of bivalve species themselves (USNRC 1980). Although not

specifically aimed at detecting sublethal effects of PAH exposure, the observations of Yevich and Barszcz (1977) on pathology in mussels (Mytilus edulis) from oiled areas of the northeastern U.S.A. suggest that the "Mussel Watch" program may be able to detect the addition of relatively large amounts of PAHs to the coastal marine environment.

To date, PAHs have not been unequivocally identified as the causative agent for cancer in any natural population of aquatic animals. Instead, the usual situation has been to find traces of PAHs in association with a myriad of other chemicals. However, there are some instances of increased tumor frequency in a variety of aquatic organisms where PAHs may have been the dominant pollutant.

A cancer-like hyperplasia was observed in the alga Porphyra tenera, cultivated in coastal water near industrial outfalls in Ohmurta, Japan (Ishio et al. 1972a). Exposure to wastewater did not induce cancer in leaves of the alga; however, exposure to bottom sediments from the river mouth in the region of the outfall for periods of 80-320 minutes resulted in cancerous growths within the next 30 days. The neutral fraction extracted from this bottom sediment (and further fractionation) resulted in the isolation of two compounds with carcinogenic potential (Ishio et al. 1972b). They were identified as benzanthrone and a hydrocarbon of molecular formula $C_{25}H_{14}$, whose structure was not elucidated (Ishio et al. 1970).

Yevich and Barszcz (1977) studied neoplasms in the soft-shell clam (Mya arenaria) from two oil-spill sites in Maine and found a high incidence of gonadal tumors from one site and of hematopoietic neoplasms at another. Laboratory studies in which clams were exposed to the types of oil found at the spill sites were performed, but the results did not substantiate the hypothesis that oil was the causative agent for the neoplasms. Brown et al. (1979) conducted a study on populations of the same species of soft-shell clam and the relationship of their associated neoplasms to PAH levels in the environment along the New England Atlantic coast. The concentration of petroleum-derived hydrocarbons in clams was related to the concentration in the associated sediments and there was a relationship between the concentration of PAHs in clams and the prevalence of neoplasms. However, a smaller percentage of clams from sites with no history of PAH pollution also showed evidence of neoplastic lesions.

Powell et al. (1970) noted ovicell hyperplasia in the bryozoan Schizoporella unicornis in colonies placed in an estuary contaminated with coal tar derivatives; however, levels of individual PAHs in the water were not measured, nor were the effects of change in salinity discussed. Straughan and Lawrence (1975) could not corroborate these findings with the same species of bryozoan exposed at various depths to natural oil seepage.

Baumann et al. (1982) noted a high incidence of hepatic tumors in the brown bullhead (Ictalurus nebulosus) population from the

Black River in Ohio, which receives large quantities of industrial effluent, compared with bullheads from a control site receiving only domestic effluent. Tissue residues of individual PAHs ranged from 0.001-6.0 $\mu g.g^{-1}$ (wet weight) and corresponded to a tumor rate of 33% in bullheads three years or older; sediment residues ranged from 5.0 (coronene) to 400 (phenanthrene) $\mu g.g^{-1}$ dry weight. At the control site, no hepatomas were observed and tissue residues of PAHs were considerably lower (0.0001-0.04 $\mu g.g^{-1}$ wet weight). The authors concluded that since the Black River differs from control sites principally in PAH levels, they are the most likely causal factor for the elevated tumor rate; however, supporting data for that position are not given.

Tiger salamander larvae (Ambystoma tigrinum) from a contaminated lagoon near the Reese Air Force Base in Texas, showed a 30 to 50% incidence of skin lesions (84 percent of which were neoplasms) in the larval population on an annual basis over a six-year period of study (Rose and Harshbarger 1977; Rose 1977). Salamanders from adjacent, uncontaminated lagoons, showed no incidence of neoplasia. Water samples were tested for the presence of putative neoplastic agents. B[a]P was found at 0.085 $\mu g.L^{-1}$ in lagoon water, and sludge from the lagoon bottom contained a number of PAHs at concentrations ranging from 0.2 to 58 $mg.kg^{-1}$ (B[a]P 0.5 $mg.kg^{-1}$) except perylene, which was present at extremely high concentrations (300 $mg.kg^{-1}$). Sewage lagoons are eutrophic and frequent large blooms of phytoplankton, Daphnia and copepods result in the accumulation of mats of dead organisms on the anoxic bottom sediments. Aizenshtat (1973) has suggested that perylene can be synthesized in a reducing environment such as this from diagenesis of natural pigments of biologic origins (see Section 3.1.2). Rose (addendum to Windsor et al. 1977) indicated that the increased incidence of neoplasia in salamander larvae was more likely related to activities at the base. Evidence that the area had been sprayed with diesel fuel (as a mosquitocide) in 1976 was cited, although this would not explain the disproportionate levels of perylene present. Other sewage lagoons, not associated with the base but prone to diagenesis of natural pigments, showed an absence of tumor-bearing animals. However, the PAH levels in these other sewage lagoons were not provided by Rose, making it impossible to identify sediment levels of PAHs in the Reese Air Force Base lagoon as a causative factor.

APPENDIX I.0

NOMENCLATURE

A. POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

The currently accepted nomenclature for PAHs is that adopted by the International Union of Pure and Applied Chemistry (IUPAC 1979). The following rules are excerpted from Nomenclature of Organic Chemistry, Section A and B (IUPAC 1979).

1. The names of polycyclic hydrocarbons with maximum number of non-cumulative double bonds end in "-ene". Trivial names which are retained may be found in IUPAC (1979).

2. The names of hydrocarbons containing five or more fused benzene rings in a straight linear arrangement end in "-acene".

3. Ortho-fused, and peri-fused polycyclic hydrocarbons with the maximum number of non-cumulative double bonds which contain at least two rings of five or more members and which have no accepted trivial name are named by prefixing to the name of a component ring or ring system (the base component) designations of the other components. The base component should contain as many rings as possible (provided it has a trivial name).

4. The attached components should be as simple as possible.

5. The prefixes designating attached components are formed by changing the ending "-ene" of the name of the component hydrocarbon into "-eno". When more than one prefix is present, they are arranged in alphabetical order.

6. Isomers are distinguished by lettering the peripheral sides of the base component a, b, c, etc., beginning with "a" for the side "1,2".

7. When a name applies equally to two or more isomeric condensed parent ring systems with the maximum number of non-cumulative double bonds and when the name can be made specific by indicating the position of one or more hydrogen atoms in the structure, this is accomplished by modifying the name with a locant, followed by italic capital H for each of these hydrogen atoms. Such symbols ordinarily precede the name. The said atom or atoms are called "indicated hydrogen".

8. For the purposes of numbering, the polycyclic system is oriented so that (a) the greatest number of rings are in the horizontal row and (b) a maximum number of rings are above and to the right of the horizontal row (upper right quadrant). If

two or more orientations meet these requirements, the one chosen is that which has as few rings as possible in the lower left quadrant. The system thus oriented is numbered in a clockwise direction, commencing with the carbon atom not engaged in ring-fusion in the most counter-clockwise position of the uppermost ring, or if there is a choice, of the uppermost ring furthest to the right, and omitting atoms common to two or more rings.

9. Atoms common to two or more rings are designated by adding roman letters "a", "b", "c", etc., to the number of the position immediately preceding[α]. Interior atoms follow the highest number, taking a clockwise sequence wherever there is a choice.

10. When there is a choice, carbon atoms common to two or more rings follow the lowest possible numbers.

11. When there is a choice, the carbon atoms which carry an indicated hydrogen atom are numbered as low as possible.

B. HETEROCYCLIC AROMATIC COMPOUNDS (HACs)

1. Ortho- and peri-fused ring compounds containing hetero atoms are named according to the fusion principle described above for hydrocarbons. When the name of a component in a fusion name contains locants (numerals or letters) that do not apply also to the numbering of the fused system, these locants are placed in square brackets. The base component should be a heterocyclic system. If there is a choice, the base component should be, by order of preference:

   (a) a nitrogen-containing component

   (b) a component containing a heteroatom (in the absence of nitrogen). The lower number is given to oxygen in preference to sulfur

   (c) a component containing the greatest number of rings

   (d) a component containing the largest possible individual ring

   (e) a component containing the greatest number of hetero atoms of any kind

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[α] Owing to limitations of word-processing equipment, neither italics nor underlining of letters between square brackets can be used.

(f) a component containing the greatest variety of hetero atoms

(g) a component containing the greatest number of hetero atoms in the order of preference nitrogen > oxygen > sulfur

(h) if there is a choice between components of the same size containing the same number and kind of hetero atoms, choose as the base component that one with the lower numbers for the hetero atoms before fusion.

2. If a position of fusion is occupied by a hetero atom, the names of the component rings to be fused are so chosen as to both contain the hetero atom.

3. In peripheral numbering of the complete fused systems, the ring system is oriented and numbered according to the principles for PAHs. When there is a choice of orientations, it is made in the following sequence in order to:

(a) give low numbers to hetero atoms (nitrogen > oxygen > sulfur)

(b) allow carbon atoms common to two or more rings to follow the lowest possible numbers

(c) give hydrogen atoms lowest possible numbers

(d) ensure that the rings are numbered as for hydrocarbons but numbers are given to all hetero atoms even when common to two or more rings. Interior hetero atoms are numbered last following the shortest path from the highest previous number.

Table I-1. Nomenclature and structure of some representative polycyclic aromatic hydrocarbons (PAHs).

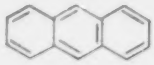
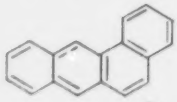
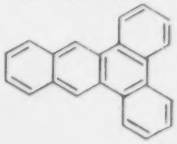
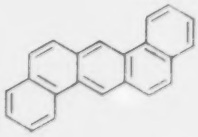
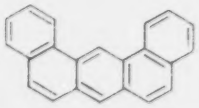
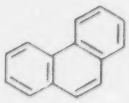
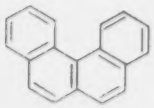
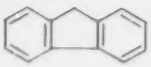
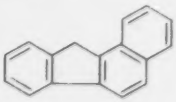
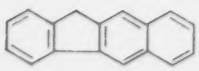
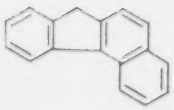
Compound Name[a] (IUPAC)	Abbreviation	Molecular Formula	Molecular Weight	Molecular Structure
1. Anthracene Series				
Anthracene	Ant	$C_{14}H_{10}$	178.2	
Benz[a]anthracene	B[a]A	$C_{18}H_{12}$	228.3	
Dibenz[a,c]anthracene	D[ac]A	$C_{22}H_{14}$	279.2	
Dibenz[a,h]anthracene	D[ah]A	$C_{22}H_{14}$	279.2	
Dibenz[a,j]anthracene	D[aj]A	$C_{22}H_{14}$	279.2	
2. Phenanthrene Series				
Phenanthrene	Phen	$C_{14}H_{10}$	178.2	
Benzo[c]phenanthrene	B[c]Phen	$C_{18}H_{12}$	228.3	
3. Fluorene Series				
Fluorene	Fl	$C_{13}H_{10}$	166.2	
Benzo[a]fluorene	B[a]Fl	$C_{17}H_{12}$	216.3	
Benzo[b]fluorene	B[b]Fl	$C_{17}H_{12}$	216.3	
Benzo[c]fluorene	B[c]Fl	$C_{17}H_{12}$	216.3	

Table I-1. (Cont'd)

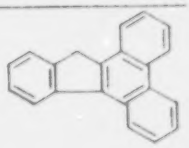
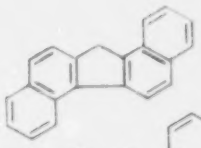
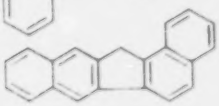
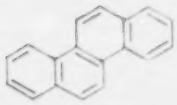
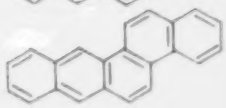
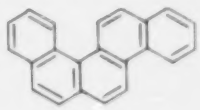
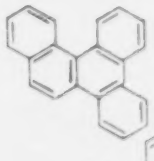
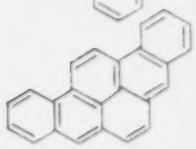
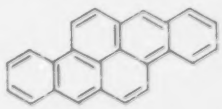
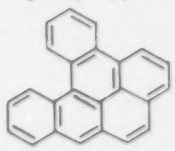
Compound Name[a] (IUPAC)	Abbreviation	Molecular Formula	Molecular Weight	Molecular Structure
Dibenzo[a,c]fluorene	DB[ac]Fl	$C_{21}H_{14}$	266.4	
Dibenzo[a,g]fluorene	DB[ag]Fl	$C_{21}H_{14}$	266.4	
Dibenzo[a,h]fluorene	DB[ah]Fl	$C_{21}H_{14}$	266.4	
4. Chrysene Series				
Chrysene	Chry	$C_{18}H_{12}$	228.3	
Dibenzo[def,mnol]chrysene (Anthanthrene)	DB[def,mnol]C	$C_{22}H_{12}$	276.3	
Benzo[b]chrysene	B[b]C	$C_{22}H_{14}$	278.4	
Benzo[c]chrysene	B[c]C	$C_{22}H_{14}$	278.4	
Benzo[g]chrysene	B[g]C	$C_{22}H_{14}$	278.4	
Dibenzo[a,def]chrysene (Benzo[rst]pentaphene)	DB[a,def]C	$C_{22}H_{14}$	278.4	
Dibenzo[b,def]chrysene (Dibenzo[a,h]pyrene)	DB[b,def]C	$C_{24}H_{14}$	278.4	
Dibenzo[def,p]chrysene (Dibenzo[a,l]pyrene)	DB[def,p]C	$C_{24}H_{14}$	278.4	

Table I-1. (Cont'd)

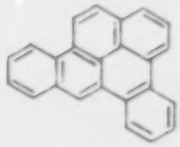
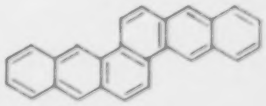
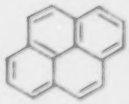
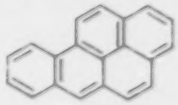
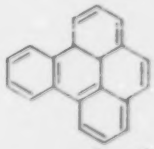
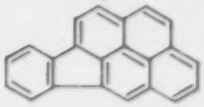
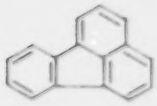
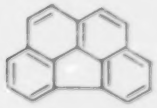
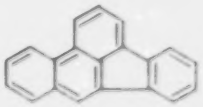
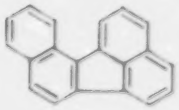
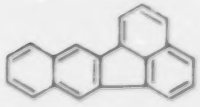
Compound Name[a] (IUPAC)	Abbreviation	Molecular Formula	Molecular Weight	Molecular Structure
Naptho[1,2,3,4-def]chrysene (Dibenzo[a,e]pyrene)	N[1,2,3,4-def]C	$C_{24}H_{14}$	278.4	
Dibenzo[b,k]chrysene	DB[b,k]C	$C_{26}H_{16}$	328.4	
5. Pyrene Series				
Pyrene	Pyr	$C_{16}H_{10}$	202.2	
Benzo[a]pyrene	B[a]P	$C_{20}H_{12}$	252.3	
Benzo[e]pyrene	B[e]P	$C_{20}H_{12}$	252.3	
Indeno[1,2,3-cd]pyrene	I[1,2,3-cd]P	$C_{22}H_{12}$	276.3	
6. Fluoranthene Series				
Fluoranthene	Flt	$C_{16}H_{10}$	202.2	
Benzo[ghi]fluoranthene	B[ghi]F	$C_{18}H_{10}$	226.3	
Benzo[b]fluoranthene	B[b]F	$C_{20}H_{12}$	252.3	
Benzo[j]fluoranthene	B[j]F	$C_{20}H_{12}$	252.3	
Benzo[k]fluoranthene	B[k]F	$C_{20}H_{12}$	252.3	

Table I-1. (Cont'd)

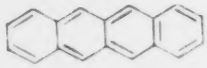
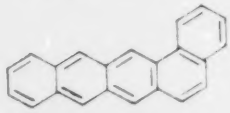
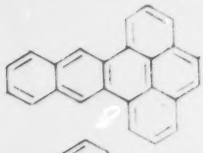
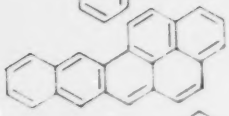
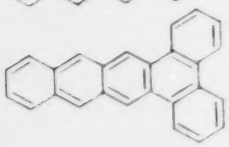
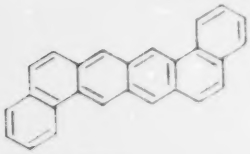
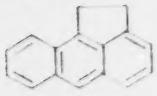
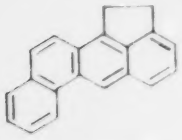
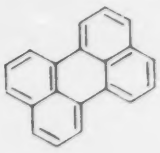
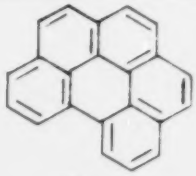
Compound Name[a] (IUPAC)	Abbreviation	Molecular Formula	Molecular Weight	Molecular Structure
7. Napthacene Series				
Naphthacene (Benzo[b]anthracene)	Nap	$C_{18}H_{12}$	228.3	
Benzo[a]naphthacene	B[a]N	$C_{22}H_{14}$	278.4	
Dibenzo[de,qr]naphthacene (Naphtho[2,3-e]pyrene)	DB[de,qr]N	$C_{24}H_{14}$	302.4	
Dibenzo[fg,op]naphthacene (Dibenzo[e,l]pyrene)	DB[fg,op]N	$C_{24}H_{14}$	302.4	
Naphtho[1,2,3-cde]naphthacene (Naphtho[2,3-a]pyrene)	N[1,2,3-cde]N	$C_{24}H_{14}$	302.4	
Dibenzo[a,c]naphthacene	DB[ac]N	$C_{26}H_{16}$	328.4	
Dibenzo[a,j]naphthacene	DB[aj]N	$C_{26}H_{16}$	328.4	
8. Aceanthrylene Series				
Aceanthrylene	Ace	$C_{16}H_{12}$	180.3	
Benzo[j]aceanthrylene (Cholanthrene)	B[j]Ace	$C_{20}H_{14}$	254.3	
9. Perylene Series				
Perylene	Per	$C_{20}H_{12}$	252.3	

Table I-1. (Cont'd)

Compound Name[a] (IUPAC)	Abbreviation	Molecular Formula	Molecular Weight	Molecular Structure
Benzo[ghi]perylene	B[ghi]Per	$C_{22}H_{12}$	276.3	
Dibenzo[ghi,pqr]perylene (Coronene)	DB[ghi,pqr]Per	$C_{24}H_{12}$	300.4	

[a] Trivial names that may appear in the literature are included in brackets.

Table I-2. Nomenclature and structure of some representative polycyclic quinones and heterocyclic aromatic compounds (HACs).

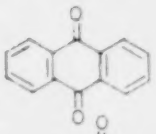
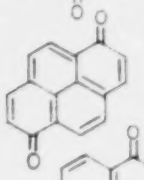
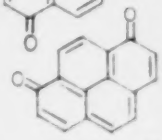
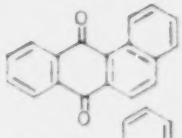
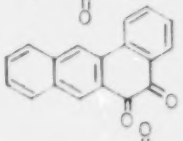
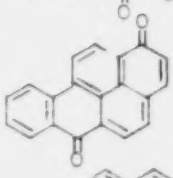
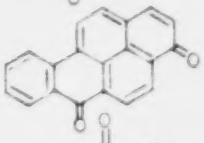
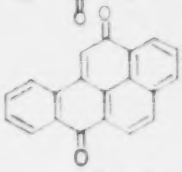
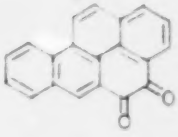
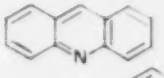
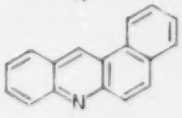
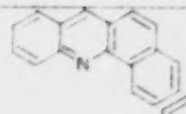
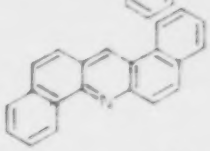
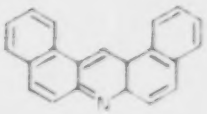
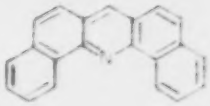
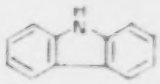
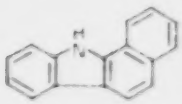
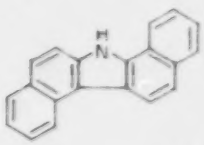
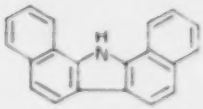
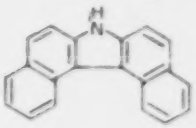
Compound Name (IUPAC)	Abbreviation	Molecular Formula	Molecular Weight	Molecular Structure
1. Quinone Series				
9,10-Anthraquinone	Anth-9,10-Q	$C_{14}H_8O_2$	208.2	
1,6-Pyrenequinone	Pyr-1,6-Q	$C_{16}H_8O_2$	232.2	
1,8-Pyrenequinone	Pyr-1,8-Q	$C_{16}H_8O_2$	232.2	
7,12-Benz[a]anthracene-quinone	B[a]A-7,12-Q	$C_{18}H_{10}O_2$	258.3	
5,6-Benz[a]anthracene-quinone	B[a]A-5,6-Q	$C_{18}H_{10}O_2$	258.3	
1,6-Benzo[a]pyrenequinone	B[a]P-1,6-Q	$C_{20}H_{10}O_2$	282.3	
3,6-Benzo[a]pyrenequinone	B[a]P-3,6-Q	$C_{20}H_{10}O_2$	282.3	
6,12-Benzo[a]pyrenequinone	B[a]P-6,12-Q	$C_{20}H_{10}O_2$	282.3	
4,5-Benzo[a]pyrenequinone	B[a]P-4,5-Q	$C_{20}H_{10}O_2$	282.3	
2. Acridine Series				
Acridine	Ac	$C_{13}H_9N$	179.2	
Benz[a]acridine	B[a]Ac	$C_{17}H_{11}N$	229.3	

Table I-2. (Cont'd)

Compound Name (IUPAC)	Abbreviation	Molecular Formula	Molecular Weight	Molecular Structure
Benz[c]acridine	B[c]Ac	$C_{17}H_{11}N$	229.3	
Dibenz[a,h]acridine	DB[ah]Ac	$C_{21}H_{13}N$	279.3	
Dibenz[a,j]acridine	DB[aj]Ac	$C_{21}H_{13}N$	279.3	
Dibenz[c,h]acridine	DB[ch]Ac	$C_{21}H_{13}N$	279.3	
3. Carbazole Series				
Carbazole	Carb	$C_{12}H_9N$	167.2	
Benzo[a]carbazole	B[a]Carb	$C_{16}H_{11}N$	217.27	
Dibenzo[a,g]carbazole	DB[ag]Carb	$C_{20}H_{13}N$	267.3	
Dibenzo[a,i]carbazole	DB[ai]Carb	$C_{20}H_{13}N$	267.3	
Dibenzo[c,g]carbazole	DB[cg]Carb	$C_{20}H_{13}N$	267.3	

APPENDIX II.0

ABSORPTION SPECTRA OF SOME POLYCYCLIC AROMATIC HYDROCARBONS

Table II-1. Absorption spectra of some polycyclic aromatic hydrocarbons (from Clar 1964).

Compound Name	Spectral Band Positions and Intensities α-Bands λ(nm)	α-Bands log ε	p-Bands λ(nm)	p-Bands Log ε	β-Bands λ(nm)	β-Bands log ε	Solvent
Fluorene	300.5	3.99	261	4.23	208	4.55	alcohol
	289	3.75					
Anthracene	-	-	374.5	3.87	251.5	5.29	methanol/ethanol
			354.5	3.86			
			338.0	3.75			
			323.0	3.47			
			308.0	3.15			
Phenanthrene	345	3.46	292.5	4.30	251	4.78	methanol/ethanol
	337	3.40	281	4.14	242	4.68	
	329.5	2.52	273.5	4.18			
	322.5	2.54					
	314	2.48					
	308.5	2.40					
Pyrene	371.5	2.40	333.5	4.71	272	4.67	methanol/ethanol
	362	2.60	318	4.47	261.5	4.40	
	356	2.71	305	4.06	251	4.04	
	351.5	2.82	292	3.62			
Fluoranthene	-	-	358.5	3.95	287	4.66	
			342	3.90	282	4.26	ethanol
			323	3.76	276	4.40	
			309	3.56	271.5	4.17	
					261.5	4.16	
					252.5	4.17	
					236(β')	4.66	
Benzo[c]phenanthrene	372	2.38	315	4.06	281	4.40	ethanol
	353	2.63	303	4.07	272	4.77	
	325.5	3.67	296	4.13	229	4.37	
					218(β')	4.70	
Benz[a]anthracene	385	3.04	359	3.76	290	5.10	benzene (ethanol)
			344	3.90	280	4.95	at 275 nm)
			329	3.90	267	4.67	
			316	3.70	254	4.62	
Chrysene	360	3.00	319	4.19	267	5.20	ethanol
	351	2.62	306	4.19	259	5.00	
	343.5	2.88	295	4.13			
			283	4.14			
Dibenz[a,c]anthracene	374	2.63	349	3.45	286	5.13	ethanol
			333	3.80	275	5.01	
			321	3.89	265	4.73	
					248	4.62	
					241	4.57	
					218(β')	4.60	
					207(β')	4.71	
Naphthacene	-	-	471	4.10	274	5.53	alcohol
			441	3.97	264.5	4.99	
			415	3.76			
			393	3.46			
			373	2.96			
			293	4.44			
Benzo[b]fluoranthene	-	-	369	3.84	301	4.54	ethanol
			350	3.98	293	4.36	
			338	3.96	289	4.36	
					276	4.36	
Benzo[k]fluoranthene	-	-	400	4.16	308	4.75	ethanol
			380	4.12	296	4.67	
			361	3.86	282	4.42	
					269	4.36	
Benzo[a]pyrene	403	3.60	384.5	4.44	264.5	4.76	ethanol
			363.5	4.36	284.3	4.66	
			347	4.10	274	4.50	
			330	3.76			

Table II-1. (Cont'd)

Compound Name	Spectral Band Positions and Intensities α-Bands λ(nm)	log ε	p-Bands λ(nm)	Log ε	β-Bands λ(nm)	log ε	Solvent
Benzo[e]pyrene	366 357 348	2.80 2.75 2.90	331.5 316.5 304	4.52 4.34 4.12	289 278 267 257	4.72 4.54 4.46 4.34	ethanol
Benzo[ghi]perylene	406.5	2.70	387.5 367 348 331	4.50 4.40 4.00 3.82	303 202	4.76 4.65	benzene (ethanol at 289 nm)
Benzo[c]chrysene	386 367 349	2.50 2.66 2.78	325 306	4.46 4.60	292.5 281 261	4.90 4.76 4.20	ethanol
Benzo[a]naphthacene	-	-	452.5 425 401 380 362	4.00 3.97 3.80 3.50 3.16	319 306	4.98 5.01	benzene
Dibenzo[b,def]chrysene	-	-	451 424 401 379	4.59 4.40 4.03 3.60	313.5 301 290	5.23 4.94 4.54	benzene
Dibenzo[def,p]chrysene	454 433 412	3.56 3.76 3.88	401 379 359	4.08 4.02 3.90	330.5 315 301 289 271 261 253 240	4.36 4.36 4.56 4.68 4.80 4.85 4.83 4.78	ethanol
Naphtho[1,2,3,4-def]chrysene	396	3.20	378 360 343 327.5	4.30 4.25 4.05 3.90	306.5 294.5	4.83 4.72	benzene
Dibenz[a,h]anthracene	344 384 374	3.01 2.61 300	350 335 322	4.16 4.23 4.28	299 289 280 223(β')	5.20 4.96 4.63 4.60	dioxane
Dibenzo[ghi,pqr]perylene	428 420 410 402 396.5 388 381.5 378 368.5	2.15 2.12 2.75 2.65 2.23 2.75 2.67 2.63 2.67	347.5 341.5 336 325.5 319.5 315.5	4.15 4.35 4.35 4.45 4.60 4.70	305 290 252 228	5.50 5.10 3.88 4.08	benzene (ethanol at 300 nm)
Dibenzo[de,qr]naphthacene	372 362 355	2.56 2.90 2.96	328 315	4.24 4.26	288 278	4.78 4.86	benzene
Dibenzo[a,c]napthacene	-	-	441.5 414 392 372 352	3.70 3.80 3.72 3.50 3.50	318 304.5 291	5.17 4.90 4.60	benzene
Dibenzo[a,j]naphthacene	-	-	437.5 411 388 368	3.88 4.00 3.88 3.70	325.5 311 298 285	5.50 5.10 4.58 4.28	benzene

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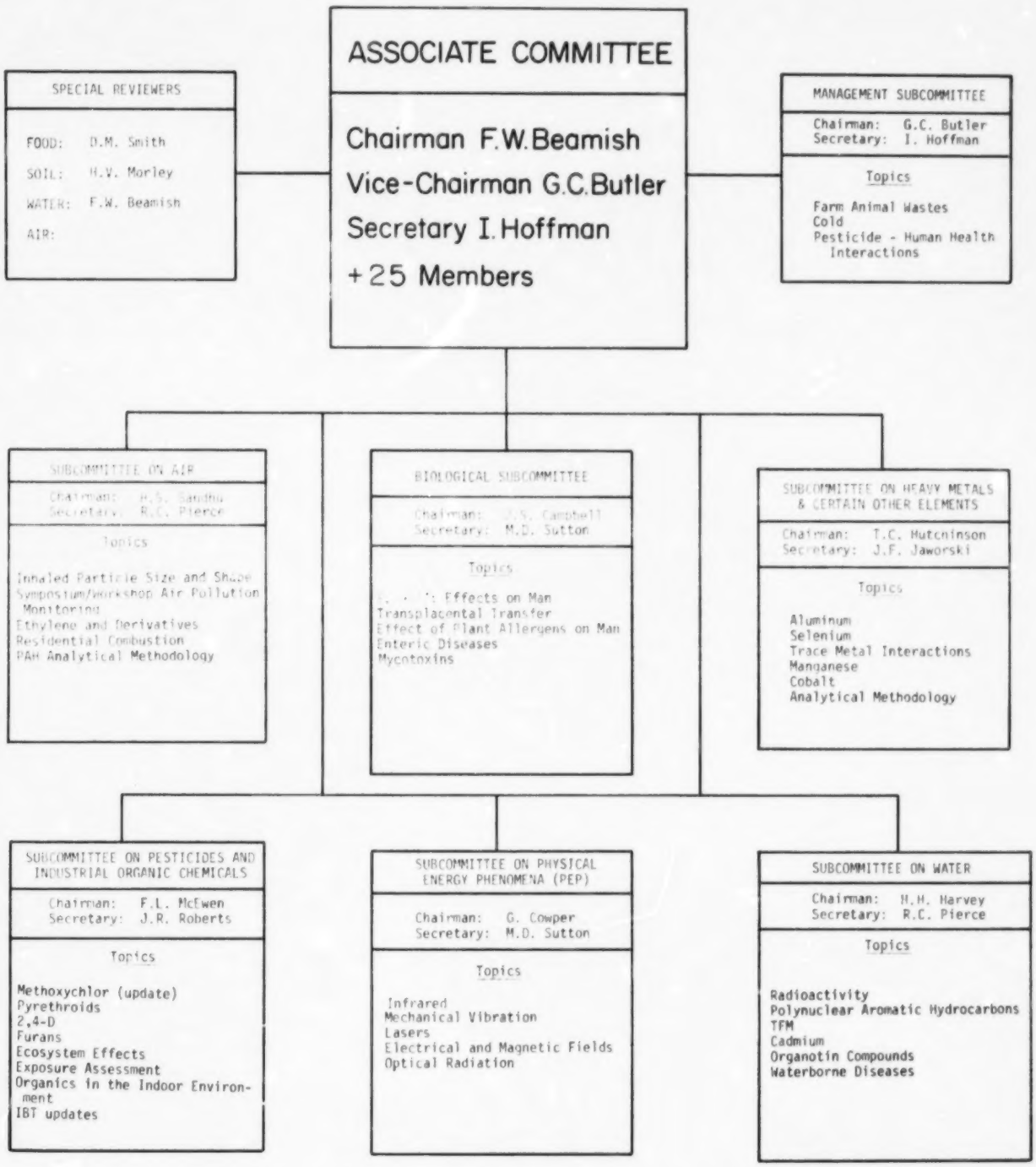

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